THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF

THE MINERALOGICAL SOCIETY

No. 224 March, 1954 Vol. XXX

A new review of the chlorites.

By Max H. Hey, M.A., D.Sc.

Department of Mineralogy, British Museum (Natural History).

[Read November 5, 1953]

THE chlorites form an extensive isostructural series with a high degree of isomorphous substitution, within which it has always been difficult to define or delimit species; until recently, owing to the lack of adequate X-ray studies, several structurally distinct species were included with the group, further complicating the problem. The group comprises aluminosilicates of magnesium and iron (ferrous and ferric); a few contain appreciable amounts of chromium, nickel, or manganese, and one (pennantite) contains manganese as a major constituent.

The first step towards the understanding of the relations of the chlorites was taken by G. Tschermak (1890, 1891), who divided them into two groups: the orthochlorites, with compositions between $(Mg,Fe'')_2Al_2SiO_5(OH)_4$ and $(Mg,Fe'')_3Si_2O_5(OH)_4$, and the leptochlorites, with compositions not explicable on this basis, and in general richer in trivalent ions (often including considerable Fe‴) relative to silicon and divalent ions. The two orthochlorite end-members have the composition of amesite and serpentine respectively, but it is now known[1] that neither of these two minerals has the chlorite structure.

The other important clue to the relations of the chlorites is the observation of A. N. Winchell (1926, 1936), confirmed by G. L. Dschang (1931) and others, that most of the leptochlorites contain considerable amounts of ferric iron, and that if their analyses are recomputed with this iron in the ferrous state they fall in line with the orthochlorites, which for their

[1] J. Orcel et al. (1950) claim that amesite is a true chlorite, but this requires confirmation. If it proves to be a valid chlorite, the following classification is not affected—a small field must be cut off for amesite.

part contain little or no ferric iron. It has been shown by Dschang and others that iron-rich orthochlorites can be oxidized by careful heating in air without change of crystal structure, and then approach in physical properties a leptochlorite of similar composition, rich in ferric iron. Winchell concludes that the chlorites are probably all strictly ferrous minerals as originally formed, but are liable to an oxidation of the type $Fe''OH \rightarrow Fe'''O$. It is possible that the few leptochlorite analyses in the literature that do not reduce to orthochlorites on recalculation of the iron to the ferrous state may all be either inaccurate analyses or analyses of mixtures or of minerals not having the chlorite structure, and that there are only two groups of chlorites, normal orthochlorites and oxidized chlorites.

A. N. Winchell (1936) proposed to classify the chlorites in terms of four end-members, antigorite $Mg_3Si_2O_5(OH)_4$ and ferroantigorite $Fe''_3Si_2O_5(OH)_4$, amesite $Mg_2Al_2SiO_5(OH)_4$, and daphnite $Fe''_2Al_2SiO_5(OH)_4$, calculating all iron as ferrous and assigning arbitrary boundaries to the several species. Unfortunately, he assigned most of his species names quite arbitrarily, without regard to the sense in which the name had been originally or normally applied, and fixed his boundaries at 20, 40, 60, and 80 molecules per cent., not of $(Mg,Fe'')_3Si_2O_5(OH)_4$ and $(Mg,Fe'')_2Al_2SiO_5(OH)_4$, but of $(Mg,Fe'')_6Si_4O_{10}(OH)_8$ and $(Mg,Fe'')_6Al_6Si_3O_{15}(OH)_{12}$; this nomenclature has never gained general acceptance.

J. Orcel (1926) collected and classified all available chlorite analyses and sought to define the several species on the basis of the original analyses and later analyses of material from the type localities. This is a sound method of approach, but a certain amount of adjustment of his arbitrary boundaries between species now seems desirable in the light of the crystal structure of the chlorites; when expressed in atoms of Si per half unit cell[1] Orcel's boundaries between groups of species fall at $2\frac{1}{2}$, $2\frac{4}{5}$, $3\frac{1}{7}$, and $3\frac{3}{11}$ atoms Si, and it is proposed to adjust the last two figures to 3·1 and 3·5; and similar rationalization of the Fe/(Mg+Fe) ratios is desirable. Moreover, neither here nor later (1950) did he distinguish the important group of oxidized chlorites.

The revised classification now proposed is shown graphically in fig. 1.

[1] Most if not all of the chlorites appear to have 36(O,OH) per unit cell, but several authors have discussed the structure and chemistry of the group on a basis of 18(O,OH), or an anhydrous basis of 14 oxygen, and it is convenient to retain this unit, which exhibits the crystallo-chemical relation of the chlorites to the micas and allied layer structures very well.

A first division of the chlorites is made into the unoxidized normal series of orthochlorites and the oxidized chlorites, and it is suggested that an arbitrary figure of 4 % Fe_2O_3 be taken as the dividing line, any chlorite with more than 4 % Fe_2O_3 being regarded as oxidized. This line is in fairly close accord with past general practice. Within the unoxidized series, grochauite, leuchtenbergite, aphrosiderite, and bavalite appear hardly worthy of species rank, and it is suggested that they should be classed as varieties of sheridanite, clinochlore, ripidolite, and daphnite respectively. A plot of the published analyses calculated to an anhydrous basis of O = 14 shows an appreciable number of points with Si less than 2·5 and high in Fe″, a field for which there has hitherto been no generally accepted name; for this field the name pseudothuringite (Koch, 1884) seems appropriate, since the mineral originally described under this name falls in the field, which corresponds to part of the field proposed for the oxidized chlorite thuringite so that the prefix pseudo- is quite appropriate.

In the oxidized series, the three accepted species delessite, chamosite,[1] and thuringite are delimited with boundaries at Si 3·1 and 2·8, corresponding to two principal boundaries in the unoxidized series. It may be found convenient to retain the name klementite as a variety of thuringite with $Mg > (Fe'' + Fe''')$; the original klementite analysis falls in this field. The boundaries now proposed for both oxidized chlorites and orthochlorites are shown in fig. 1.

[1] Recent work by G. W. Brindley and R. F. Youell (1949, 1950, 1953) shows that the material hitherto called chamosite includes at least three and probably four distinct minerals: by far the commonest 'chamosite', including that from Frodingham, Lincolnshire (no. 72 below), is not a chlorite at all, consisting of an intergrowth in varying proportions of two structurally distinct phases, one monclinic and the other orthorhombic, both of which are based on kaolin-type layers; chamosite from the type locality and the magnesium-rich varieties from Wickwar, Gloucestershire, and Brinton's quarry, West Chester, Pennsylvania (nos. 73 and 71, below) appear to be true chlorites with d_{001} 14·2 Å. and a monoclinic unit cell, like most of the chlorites so far examined in detail; 'chamosite' from Schmiedefeld, Thuringia (no. 70, below), appears to have a closely allied orthorhombic structure based on the same type of triple layer as the other true chlorites.

These complex relations raise considerable difficulties in nomenclature, particularly as the commonest and best known 'chamosites' differ structurally from the original chamosite of Chamoson. In the present paper, the term chamosite is used for the true chlorites, excluding the unnamed kaolin-type minerals (though data for at least one of the latter have been included in deriving the regression equations cited below, this is not likely to cause any appreciable errors). But it is suggested that the best solution might well be to give new names to both the chlorite and kaolin-type structures, if not to all four structurally distinct phases, and to use the name chamosite as an inclusive term like limonite, or as an ore-name, like bauxite.

The manganese-bearing chlorites include the remarkable species pennantite, chemically a klementite with the magnesium almost wholly replaced by manganese, and two varieties with small percentages of MnO; grängesite, a manganiferous brunsvigite; and manganese-pennine.

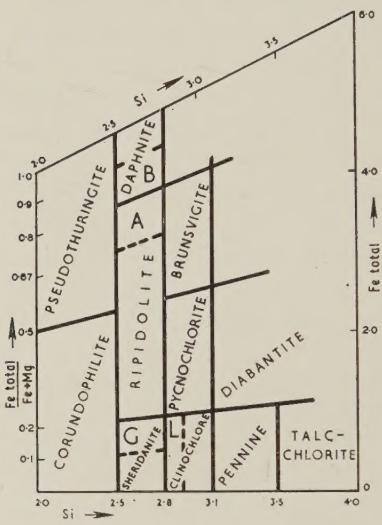


FIG. 1*a*

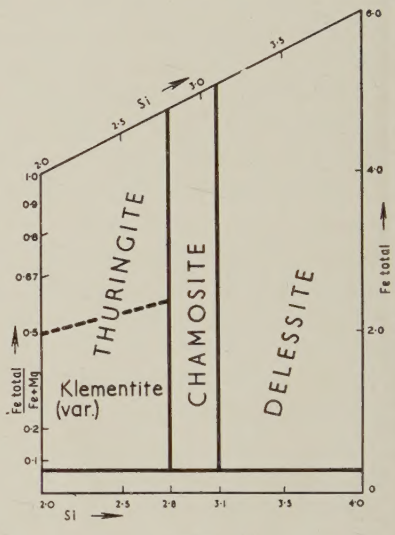


FIG. 1*b*

FIG. 1*a*. The orthochlorites, on basis of 14 oxygen (anhydrous), showing the proposed species and variety boundaries. L = Leuchtenbergite, var. of Clinochlore; G = Grochauite, var. of Sheridanite; A = Aphrosiderite, var. of Ripidolite; B = Bavalite, var. of Daphnite.

FIG. 1*b*. The oxidized chlorites ($Fe_2O_3 > 4$ %) on basis of 14 oxygen (anhydrous) calculating all iron as ferrous.

The chromiferous chlorites include three varieties: kämmererite, a variety of pennine; chrome-clinochlore, with less than 4 % Cr_2O_3; and kochubeïte, a variety of clinochlore with more than 4 % Cr_2O_3.

The following are doubtful species; if they are really chlorites and the analyses are trustworthy, they form a third division of true leptochlorites, in which the total cations are less than 10 per 14 oxygen (anhydrous basis): batavite, epichlorite, epiphanite,[1] moravite, parathuringite, phyllochlorite, steatargillite, and strigovite. Mackensite and viridite (of Kretschmer), according to their discoverer, grade continu-

[1] X-ray photographs show that epiphanite is a chlorite; the one analysis would place it as a true leptochlorite, but the analysis may be inaccurate and it may prove to be a diabantite.

ously into thuringite; if they are really chlorites and the analyses are trustworthy, they are of a type otherwise unknown, viridite being an orthochlorite containing considerable ferric iron, near $Fe''_5Fe'''Si_2AlO_{10}(OH)_8$, and mackensite the corresponding oxidized chlorite, near $Fe'''_6Si_3AlO_{15}(OH)_3$.

A number of supposed species can safely be rejected on the basis of the original descriptions and analyses (if they are truly chlorites); berlauite, chloropite, euralite, and hallite (of Leeds) are delessite; metachlorite falls within the field now allotted to bavalite, which is the older name; subdelessite is a magnesian chamosite; rumpfite[1] included some sheridanites and some leuchtenbergites; pseudophite is in part clinochlore and in part pennine; loganite is a pseudomorph of pennine after amphibole; pyrosclerite a pseudomorph of pennine after pyroxene.

In 1926, A. N. Winchell attempted to show the variation of the optical properties of the chlorites with their chemical composition, and revised this plot in 1936 to include new data, but even so his plot was only based on 43 points; since then, much new data has accumulated, and 108 points are now available for the derivation of a relation between composition and refractive index, and 81 for birefringence; it therefore appeared opportune to revise the variation graphs. Temporarily rejecting 7 refractive index and 5 birefringence determinations on chromiferous chlorites, and assuming a linear correlation of the physical properties with the ferrous and ferric iron and the silica content,[2] regression equations were derived by the method of least squares, and the mean variance of the residuals was also calculated. The results gave, on the whole, gratifying agreement, especially in view of the very approximate nature of most of the birefringence data; the biggest departures from the regression equation were shown by a chamosite and two thuringites near the chamosite-thuringite boundary, and it is possible that these were not really chlorites. The equations are given below, while the departures from them are shown graphically in figs. 2 and 3; in fig. 2, the departures of the observed data from the calculated values are plotted against the number of silicon atoms per unit cell, and in fig. 3, against the total number of iron atoms per unit cell and against the number of ferric ions.

[1] A. Hödl (1941, p. 59) gives a thorough review of rumpfite, and rejects it as a superfluous and often misapplied name.

[2] Three parameters suffice to define the composition of an orthochlorite or oxidized chlorite, and Si, total Fe (Fe^t), and Fe''', in atoms per 14 oxygen (anhydrous basis, all iron calculated as ferrous), have proved a convenient choice. If the correlation with these parameters is linear, it will be linear with any comparable choice of parameters.

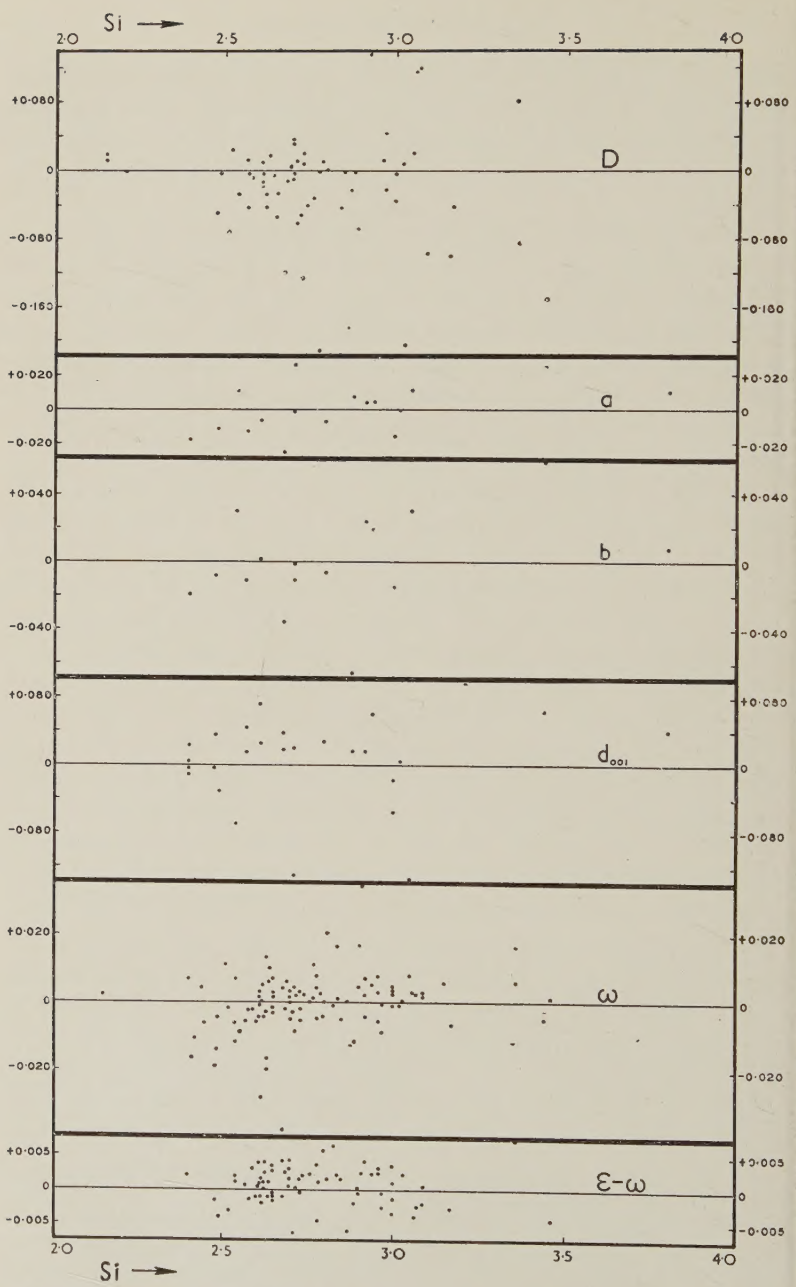


FIG. 2. Departures of observed physical data from the values calculated from the regression equations, in relation to the silica content.

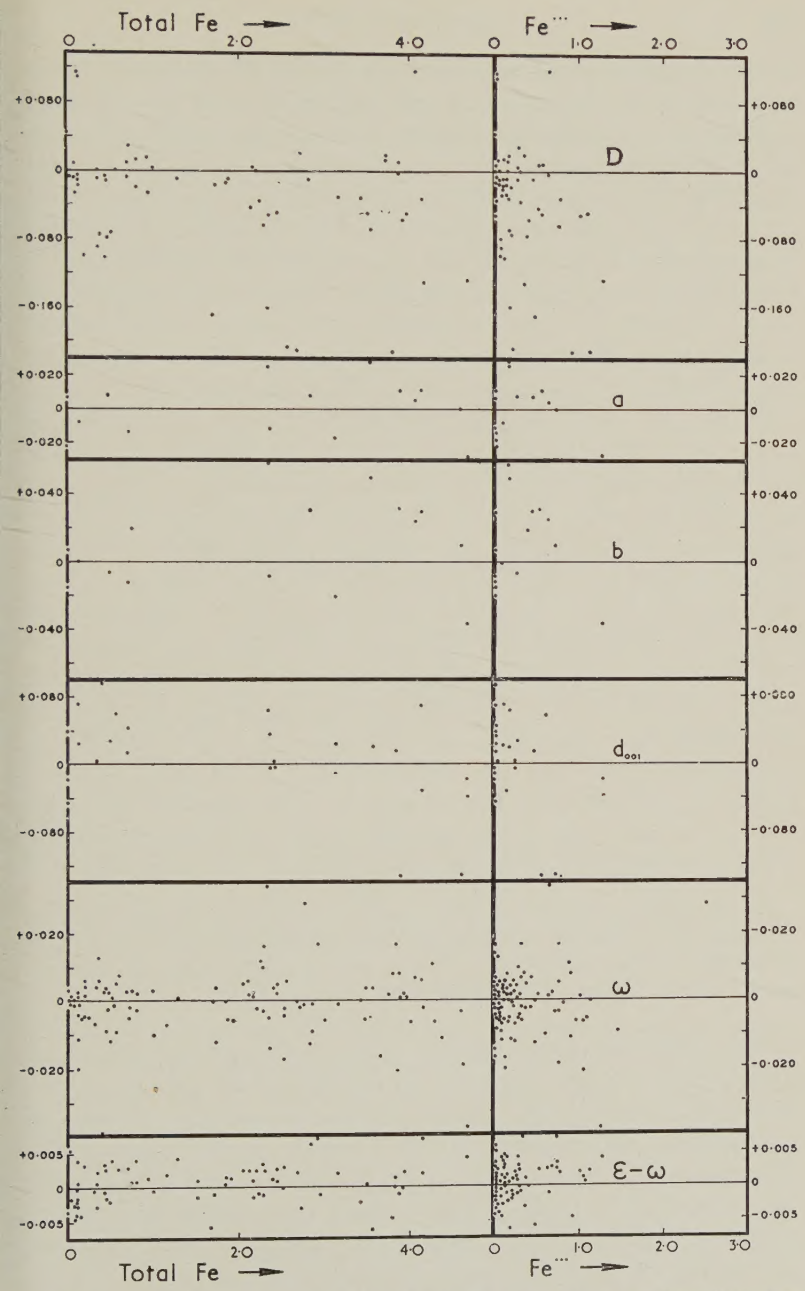


FIG. 3. Departures of observed physical data from the values calculated from the regression equations in relation to the total iron content (left), and to the ferric iron content (right).

It will readily be seen that there is nothing to suggest any notable departure from linear correlation, or any serious error in the regression coefficients calculated. The variations in birefringence and in refractive index with Si and total Fe are shown graphically in fig. 4. As compared with Winchell's diagram (1936, fig. 1), the most notable difference is in the birefringence, for which Winchell derives a non-linear correlation; there is no direct evidence for non-linear correlation, and it is usual to assume linear correlation until evidence to the contrary is obtained.

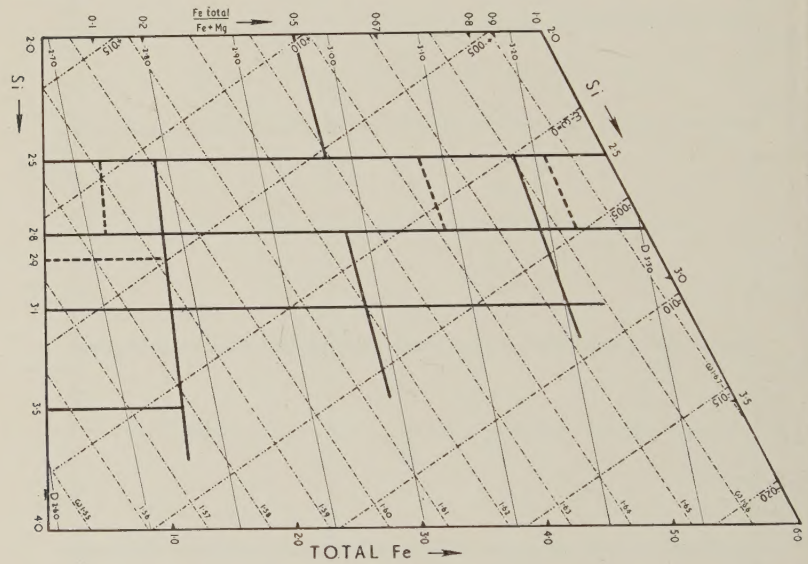


Fig. 4. Refractive index (ω), birefringence ($\epsilon-\omega$), and specific gravity (D) of orthochlorites in relation to composition. For oxidized chlorites, ω and D are higher and $\epsilon-\omega$ lower, in proportion to the percentage of Fe_2O_3. The boundaries of the orthochlorite species and varieties are shown.

Eight refractive index determinations and six birefringences are available on analysed chromiferous chlorites. The accuracy of the birefringence data is not sufficient to establish any definite effect of chromium on this property; Winchell believed he had evidence of a decrease in $\epsilon-\omega$ with increase of Cr, but the evidence for this is not adequate. There is, however, clear evidence of an increase in the refractive index with increase in Cr, at least comparable with the effect of Fe‴, and an approximate regression coefficient has been calculated.

From the available data on pennantite, Mn would appear to have

much the same effect as Fe″ in the refractive index, increasing it, and an effect between those of Fe″ and Fe‴ on the birefringence, decreasing $\epsilon - \omega$. None of the other manganiferous chlorites for which optical data are available contains much manganese and for these small amounts its effect may be put equal to that of iron. The regression coefficients cited below are derived from the observations on pennantite.

W. von Engelhardt (1942), from X-ray data on three chlorites, believed he had evidence of a decrease in the cell side c and an increase in b with increase in iron content. F. A. Bannister and W. F. Whittard (1945) obtained clear evidence of an increase in c and in the related d_{001} with increase in Si. Regression equations have been calculated from all available X-ray data (twenty analyses with associated determinations of d_{001} and sixteen with determinations of a and b). From these it is quite clear that d_{001} increases with increase of Si, presumably owing to weaker inter-layer bonding, is independent of the Fe″ content, within the accuracy of measurement, but decreases slightly with increase of Fe‴, presumably owing to stronger inter-layer bonding; both a and b are independent of the Si content, but increase with increase of Fe″ or Fe‴; the effects of Fe″ and Fe‴ are equal within the accuracy of measurement, since when total Fe and Fe‴ are used as parameters, a and b appear to be independent of the latter. The expansions produced in a and b by increase in total Fe are proportional to the lengths of these axes within the accuracy of measurements. As with the optical data, the departures of the observed data from the regression equations for the cell-dimensions are plotted against Si, against total Fe, and against Fe‴ in figs. 2 and 3.

A comparison with the cell-dimensions of pennantite gives approximate values for the effect of Mn, which are included in the regression equations below; the effect proves to be an expansion in all three dimensions, and is presumably due to the greater diameter of Mn″ (Fe″ 0·72, Mg″ 0·75, Mn″ 0·91 Å.); again, the expansions produced in a and b are proportional to the lengths of these axes. There are no data at present available on the effect of Cr on the cell-dimensions of the chlorites.

From the atomic weights and the regression equations for the three cell-sides an equation for the theoretical density was calculated. This proved to give good agreement with the observed data, as may be seen from figs. 2 and 3, but it does not supply a further test of the regression equations for the cell-sides, since the differences in atomic weights supply the major element in each coefficient. As is to be expected, the observed densities tend to be rather lower than the theoretical.

The regression equations for the physical properties in terms of the

composition[1] are given below, together with the mean standard deviation[2] of the observed data; the standard deviation is given both in direct measure and as a percentage of the mean value of the physical property except in the case of the birefringence.

	$\hat{\sigma}$.	$\hat{\sigma}$ %.
$d_{001} = 13{\cdot}925 + 0{\cdot}23\ (Si-2) - 0{\cdot}05\ Fe''' + 0{\cdot}05\ Mn$	0·059	0·42
$a = 5{\cdot}320 + 0{\cdot}016\ Fe^t + 0{\cdot}027\ Mn$		
$= 5{\cdot}320\ (1 + 0{\cdot}00304\ Fe^t + 0{\cdot}0051\ Mn)$	0·015	0·28
$b = 9{\cdot}202 + 0{\cdot}028\ Fe^t + 0{\cdot}047\ Mn$		
$= 9{\cdot}202\ (1 + 0{\cdot}00304\ Fe^t + 0{\cdot}0051\ Mn)$	0·028	0·30
$D = 2{\cdot}694 - 0{\cdot}061\ (Si-2) + 0{\cdot}136\ Fe^t + 0{\cdot}010\ Fe''' + 0{\cdot}110\ Mn$	see footnote 3.	
$\omega = 1{\cdot}5954 - 0{\cdot}0263\ (Si-2) + 0{\cdot}0208\ Fe^t + 0{\cdot}0035\ Fe''' + 0{\cdot}019\ Mn + 0{\cdot}03\ Cr$	0·0100	0·63
$\epsilon - \omega = 0{\cdot}0170 - 0{\cdot}0096\ (Si-2) - 0{\cdot}00335\ Fe^t - 0{\cdot}0048\ Fe''' - 0{\cdot}006\ Mn$	0·003	—

TABLE I. List of the analyses and physical determinations on which the regression equations are based. (The species names are given on the nomenclature now proposed, fig. 1; names in parentheses are the names under which the mineral was originally described.)

Pennine

1. Zillerthal, Tyrol, Austria. (Tschermak, 1891; Orcel, 1927, no. 204; Hutton, 1947.)
2. Nottingham, Chester County, Pennsylvania. (Shannon and Wherry, 1922; Orcel, 1927, no. 249; Winchell, 1936, no. 16.)
3. Valle de Secchia, Emilia, Italy. (Bertolani, 1949.)
4. Recess, County Galway, Ireland. (Hutchinson and Smith, 1912; Orcel, 1927, no. 188; Winchell, 1936, no. 17.)
5. Locality unknown. (Dschang, 1931; Winchell, 1936, no. 23.)

Diabantite

6. Farmington Hills, Hartford County, Connecticut. (Hawes, 1875; Orcel, 1927, no. 230; Bannister and Whittard, 1945.)
7. Murlough Bay, Ballycastle, County Antrim, Ireland. (Tomkeieff, 1943.)

Clinochlore

8. Bernstein, Burgenland, Austria. (Smith, 1924; Orcel, 1927, no. 179; Bannister and Whittard, 1945.)

[1] In atoms per 14 oxygen, anhydrous basis, calculating all iron as ferrous; Fe^t is the total iron, Fe''' the ferric.

[2] The standard deviation, σ, of a series of experimental values is the square root of the mean of the squares of their departures from the true value; when the true value is not known, the estimated standard deviation, $\hat{\sigma}$, must be used, and is the square root of the mean of the squares of the departures of the experimental values from their mean, or, in the case of a regression equation, from the values given by the equation.

[3] This calculated regression equation is subject to a standard deviation of 0·016 = 0·60 % from the standard deviations of the equations for the cell-sides. The observed values are preponderantly low.

9. Philipsburg, Granite County, Montana. (Leuchtenbergite.) (Shannon, 1923; Orcel, 1927, no. 166; McMurchy, 1934; Winchell, 1936, no. 21; Gruner, 1944.)
10. Korea. (Leuchtenbergite.) (Satô, 1933; Winchell, 1936, no. 19.)
11. Korea. (Leuchtenbergite.) (Kinosaki, 1932; Winchell, 1936, no. 26.)
12. Mt. Ampanobe, Madagascar. (Lacroix, 1922; Orcel, 1927, no. 55; Winchell, 1936, no. 25.)
13. Red Mountain, Westland, New Zealand. (Hutton, 1936.)
14. Urals. (Leuchtenbergite.) (Dschang, 1931; Winchell, 1936, no. 20.)
15. Muruhatten, Jämtland, Sweden. (Du Rietz, 1935.)
16. Piedmont, Italy. (Rondolino, 1936.)
17. Dobrog Polya, Serbia, Jugoslavia. (Tajder, 1938.)
18. Besofotra, Madagascar. (Orcel, 1927, no. 170; Winchell, 1936, no. 24.)

Leuchtenbergite (var. of Clinochlore)

19. Westtown, Chester County, Pennsylvania. (Clinochlore.) (Dschang, 1931; Winchell, 1936, no. 23.)
20. Midongy, Madagascar. (Orcel, 1927, no. 47; Winchell, 1936, no. 29.)
21. Sierra de la Capelada, Galicia, Spain. (Garrido, 1949.)
22. Kings River, Fresno County, California. (Clinochlore.) (Durrell and Macdonald, 1939.)

Pycnochlorite

23. Old West mine, Penhalonga, Southern Rhodesia. (Prochlorite.) (Macgregor, 1941.)
24. Eilean Traighe, Tayvallich, Argyllshire, Scotland. (Prochlorite.) (Wiseman, 1934.)

Brunsvigite

25. Goose Creek, Loudoun County, Virginia. (Shannon, 1924.)
26. Mourne Mtns., County Down, Ireland. (Daphnite.) (Nockolds and Richey, 1939.)
27. Westfield, Hampden County, Massachusetts. (Diabantite.) (Orcel, 1927, no. 122; Winchell, 1936, no. 5.)

Sheridanite

28. Miles City, Custer County, Montana. (Shannon and Wherry, 1922; Orcel, 1927, no. 34; Winchell, 1936, no. 32; Gruner, 1944.)
29. Ambatofinandrahana, Madagascar. (Ripidolite.) (Orcel, 1927, no. 71; Winchell, 1936, no. 28.)
30. Kaintaleck, Styria, Austria. (Leuchtenbergite.) (Hödl, 1941.)
31. Oberdorf, St. Kathrein, Styria, Austria. (Leuchtenbergite.) (Hödl, 1941.)
32. Kaslinski, Urals. (Grochauite.) (Pavlovitch, 1931; Winchell, 1936, no. 30.)
33. Madison County, North Carolina. (Ripidolite.) (Orcel, 1927, no. 57; Winchell, 1936, no. 33.)
34. Brinton's quarry, West Chester, Chester County, Pennsylvania. (Colerainite.) (Shannon and Wherry, 1922; Orcel, 1927, no. 32; Winchell, 1936, no. 37.)
35. Sheridan County, Wyoming. (Wolff, 1912; Orcel, 1927, no. 33; Winchell, 1936, no. 38.)

Grochauite (var. of Sheridanite)

36. Burra Burra, Ducktown, Polk County, Tennessee. (McMurchy, 1934; Gruner, 1944.)

37. Modena, Italy. (Ripidolite.) (Gallitelli, 1929; Winchell, 1936, no. 27.)
38. Achmatovsk, Urals. (Clinochlore.) (Dschang, 1931; Winchell, 1936, no. 35.)
39. Regné, Bihain, Luxembourg, Belgium. (Mélon, 1938.)
40. Haüselberg, Loeben, Styria, Austria. (Hödl, 1941.)
41. Rainbow Camp, Leysdorp, Transvaal. (Ripidolite.) (Orcel, 1927, no. 68; Winchell, 1936, no. 31.)
42. Antohidrano, Madagascar. (Orcel, 1927, no. 67; Winchell, 1936, no. 36.)
43. Madison County, North Carolina. (Ripidolite.) (Orcel, 1927, no. 58; Winchell, 1936, no. 31.)

Ripidolite

44. Coronet Peak, Wakatipu, Otago, New Zealand. (Hutton, 1938.)
45. Holleton, South-West Division, Western Australia. (Corundophilite.) (Simpson, 1936.)
46. Aorere, Nelson, New Zealand. (Hutton and Seelye, 1945.)
47. Isère, France. (Orcel, 1927, no. 95; Winchell, 1936, no. 6.)
48. Piz Urschaid, Silvretta, Tyrol, Austria. (Hödl, 1941.)
49. Springburn, Kawarau, Otago, New Zealand. (Hutton, 1938.)
50. Androta, Madagascar. (Orcel, 1927, no. 93; Winchell, 1936, no. 13.)
51. Masoala, Madagascar. (Orcel, 1927, no. 82; Winchell, 1936, no. 7.)
52. Laifour, Ardennes, France. (Orcel, 1927, no. 81; Winchell, 1936, no. 9.)
53. Field, British Columbia. (Aphrosiderite.) (Larsen and Steiger, 1917; Orcel, 1927, no. 98; Winchell, 1936, no. 12.)
54. Hawleyville, Fairfield County, Connecticut. (Agar and Emendorfer, 1937.)
55. Valais, Switzerland. (Dschang, 1931; Winchell, 1936, no. 8.)
56. Black Bear claim, Shoshone County, Idaho. (Shannon, 1926; Winchell, 1936, no. 10.)
57. Waterworks tunnel, Washington, District of Columbia. (Clarke and Schneider, 1891; Larsen, 1920; Shannon, 1920; Orcel, 1927, no. 78; Winchell, 1936, no. 14.)

Aphrosiderite (var. of Ripidolite)

58. Tolgus mine, Penzance, Cornwall. (Daphnite.) (Hallimond, 1939; Bannister and Whittard, 1945.)
59. Weilburg, Nassau, Germany. (Orcel, 1927, no. 123; Winchell, 1936, no. 4.)

Bavalite (var. of Daphnite)

60. Bas Vallon, Forêt de Lorges, Quintin, Côtes-de-Nord, France. (Orcel, 1927, no. 128; Winchell, 1936, no. 2; von Engelhardt, 1942.)

Daphnite

61. Penrhyn quarry, Llandegai, Carnarvonshire, Wales. (Thuringite.) (Pulfrey, 1933; Bannister and Whittard, 1945.)

Corundophilite

62. Chester, Hampden County, Massachusetts. (The mean of six analyses was used.) (Orcel, 1927, nos. 3, 4, 5, 6, 7, and 8; Gruner, 1944; Bannister and Whittard, 1945.)
63. Comberousse, Savoy, France. (Sheridanite.) (Orcel, 1927, no. 31; Winchell, 1936, no. 39.)

Pseudothuringite

64. Granitzer, Weiz, Styria, Austria. (Ripidolite.) (Hödl, 1941.)
65. Togo, Lembi County, Idaho. (Shannon, 1926.)

66. Sherman mine, Shoshone County, Idaho. (Shannon, 1926.)
67. Idval, north Urals. (Lyamina and Soboleva, 1937.)
68. Bolivia. (McMurchy, 1934; Gruner, 1944.)

Delessite

69. Challis, Custer County, Idaho. (A manganiferous variety.) (Shannon, 1926.)

Chamosite (nos. 70, 71, and 73 are true chlorites; some of the others may not be chlorites, see footnote on p. 279; no. 72 is not a chlorite).

70. Schmiedefeld, Thuringia, Germany. (Jung, 1931; von Engelhardt, 1942.)
71. Brinton's quarry, West Chester, Chester County, Pennsylvania. (Shannon and Wherry, 1922; McMurchy, 1933.)
72. Frodingham, Lincolnshire. (Hallimond, 1939; Bannister and Whittard, 1945.)
73. Wickwar, Gloucestershire. (Bannister and Whittard, 1945.)
74. Ernsthausen, Lahn, Germany. (Aphrosiderite.) (Holzner, 1938.)
75. Wołowiec, Tatra Mountains, Poland. (Kozik, 1930.)
76. Słowkowska valley, Tatra Mountains, Poland. (Kozik, 1930.)
77. Lembecq, Brabant, Belgium. (Mélon, 1938.)
78. Eppstein, Lahn, Germany. (Thuringite.) (Holzner, 1938.)

Klementite (var. of Thuringite)

79. Vals, Graubünden, Switzerland. (Ripidolite.) (Jakob and de Quervain, 1939.)
80. Vielsalm, Luxembourg, Belgium. (Mélon, 1938.)
81. Messina, Transvaal. (Thuringite.) (Orcel, 1927, no. 9; Winchell, 1936, no. 11.)
82. Val Cristallina, Val Medels, Graubünden, Switzerland. (Ripidolite.) (Jakob and de Quervain, 1939.)

Thuringite

83. Zirmsee, Rauris, Carinthia, Austria. (von Zepharovich, 1877; Orcel, 1927, no. 20; von Engelhardt, 1942.)
84. Schmiedefeld, Thuringia. (The mean of five analyses was used.) (Orcel, 1927, nos. 11, 12, 18, and 24; Jung and Kohler, 1930; von Engelhardt, 1942; Bannister and Whittard, 1945.)
85. Creede, Mineral County, Colorado. (Larsen and Steiger, 1917; Orcel, 1927, no. 28; Winchell, 1936, no. 1.)
86. Evisa, Corsica. (Orcel, 1927, no. 25; Winchell, 1936, no. 3.)
87. Weilburg, Lahn, Germany. (Aphrosiderite.) (Holzner, 1938.)
88. Kalgoorlie, Western Australia. (Simpson, 1937.)
89. Randalls, Western Australia. (Daphnite.) (Simpson, 1936.)
90. Schottgraben, Frohnleiten, Styria, Austria. (Ripidolite.) (Hödl, 1941.)
91. Nil-St.-Vincent, Brabant, Belgium. (Mélon, 1938.)
92. Fortuna mine, Lahn, Germany. (Holzner, 1938.)
93. Allerheiligenbauen, St. Jakob, Breitenau, Styria, Austria. (Hödl, 1941.)
94. Georg-Joseph mine, Lahn, Germany. (Aphrosiderite.) (Holzner, 1938.)
95. Klein-Litzner, Silvretta, Tyrol, Austria. (Hödl, 1941.)
96. Serpont Recogne, Luxembourg, Belgium. (Mélon, 1938.)
97. Rötzgraben, Trofaiach, Styria, Austria. (Hödl, 1941.)
98. Goldzeche, Rauris, Carinthia, Austria. (Hödl, 1941.)
99. Mt. Satirst, North-West Division, Western Australia. (Simpson, 1937.)
100. Zirmsee, Rauris, Carinthia, Austria. (A manganiferous variety.) (Hödl, 1941.)
101. Artificial, produced by heating no. 55 in air. (Dschang, 1931; Winchell, 1936, no. 8a.)

Manganese-pennine (var. of Pennine)

102. Långban, Sweden. (von Eckermann, 1927.)
103. Långban, Sweden. (von Eckermann, 1927.)

Pennantite

104. Benallt mine, Carnarvonshire, Wales. (Smith, Bannister, and Hey, 1946.)

Kämmererite (var. of Pennine)

105. Deer Park, Wyoming. (Shannon, 1920; Orcel, 1927, no. 285; Winchell, 1936, no. 2.)
106. Locana, Piedmont, Italy. (Sanero, 1933.)
107. Säkok Ruopsok, Jämtland, Sweden. (Du Rietz, 1935; Winchell, 1936, no. 7.)

Chrome-clinochlore (var. of Clinochlore)

108. Kaukapakapa, North Auckland, New Zealand. (Leuchtenbergite.) (Hutton and Seelye, 1947.)
109. Patevi, Togoland, West Africa. (Clinochlore.) (Orcel, 1927, no. 272; Winchell, 1936, no. 22.)
110. Newcastle, Eldorado County, California. (Kämmererite.) (Shannon, 1920; Orcel, 1927, no. 266.)
111. Mount Albert, Schickshock Mts., Quebec. (Osborne and Archambault, 1948.)

Kochubeite (var. of Clinochlore)

112. Patevi, Togoland, West Africa. (Orcel, 1927, no. 271; Winchell, 1936, no. 4.)
113. Kraubath, Styria, Austria. (Kopetzky, 1948.)

Leptochlorites (low cation totals, below 5·6 per 14 oxygen)

114. Kropfmühle, Passau, Bavaria. (Batavite.) (Weiss and Hofmann, 1951.)
115. Calton Hill, Derbyshire. (Delessite.) (Tomkeieff, 1926.)
116. Sungul, Urals. (Sokolov, 1931.)
117. Long Hill, Trumbull, Fairfield County, Connecticut. (Ripidolite.) (McMurchy, 1933; Orcel, 1927, no. 102; Gruner, 1944. For a discussion of the possible constitution of this abnormal chlorite, see Gruner, 1944.)

References.

Agar (W. M.) and Emendorfer (E. H.), 1937. Amer. Journ. Sci., ser. 5, vol. 34, p. 77. [M.A. **7**–258.]

Bannister (F. A.) and Whittard (W. F.), 1945. Min. Mag., vol. 27, p. 99.

Bertolani (M.), 1949. Mem. Comit. Sci. Centr. Club. Alpino Italiano, Modena, no. 1. [M.A. **11**–51.]

Brindley (G. W.), 1949. Nature, vol. 164, p. 319. [M.A. **11**–104.]

—— 1951. Min. Mag., vol. 29, p. 502.

—— and Ali (S. Z.), 1950. Acta Cryst. Cambridge, vol. 3, p. 25. [M.A. **11**–104.]

—— and Youell (R. F.), 1953. Min. Mag., vol. 30, p. 57.

Clarke (F. W.) and Schneider (E. A.), 1891. Bull. U.S. Geol. Surv., no. 78, p. 19.

Dschang (G. L.), 1931. Chemie der Erde, vol. 6, p. 416. [M.A. **5**–39.]

Du Rietz (T.), 1935. Geol. För. Förh. Stockholm, vol. 57, p. 133. [M.A. **6**–216.]

Durrell (C.), and Macdonald (G. A.), 1939. Amer. Min., vol. 24, p. 452. [M.A. **7**–551.]

Eckermann (H. von), 1927. Geol. För. Förh. Stockholm, vol. 49, p. 450. [M.A. **3**-474.]
Engelhardt (W. von), 1942. Zeits. Krist., vol. 104, p. 142. [M.A. **8** 291.]
Gallitelli (P.), 1929. Atti Soc. Nat. Mat. Modena, ser. 6, vol. 8 (60), p. 86. [M.A. **4**-470.]
Garrido (J.), 1949. Bull. Soc. Franç. Min. Crist., vol. 72, p. 549. [M.A. **11**-104.]
Gruner (J. W.), 1944. Amer. Min., vol. 29, p. 422. [M.A. **9**-232.]
Hallimond (A. F.), 1939. Min. Mag., vol. 25, p. 441.
Hawes (G. W.), 1875. Amer. Journ. Sci., ser. 3, vol. 9, p. 454.
Hödl (A.), 1941. Neues Jahrb. Min., Beil.-Bd. 77, p. 1. [M.A. **8**-304.]
Holzner (J.), 1938. Neues Jahrb. Min., Beil.-Bd. 73, p. 389. [M.A. **7**-408.]
Hutchinson (A.) and Smith (W. Campbell), 1912. Min. Mag., vol. 16, p. 264.
Hutton (C. O.), 1936. Trans. Roy. Soc. New Zealand, vol. 66, p. 35. [M.A. **6**-364.]
—— 1938. Min. Mag., vol. 25, p. 198.
—— and Seelye (F. T.), 1945. Trans. Roy. Soc. New Zealand, vol. 75, p. 160. [M.A. **9**-268.]
—— —— 1947. Ibid., vol. 76, p. 481. [M.A. **10**-271.]
Jakob (J.) and Quervain (F. de), 1939. Schweiz. Min. Petr. Mitt., vol. 19, p. 307. [M.A. **8**-92.]
Jung (H.) and Kohler (E.), 1930. Chemie der Erde, vol. 5, p. 182. [M.A. **4**-334.]
—— 1931. Ibid., vol. 6, p. 275. [M.A. **5**-40.]
Kinosaki (Y.), 1932. Bull. Min. Survey Chosen, vol. 7, no. 1. [M.A. **5**-421.]
Kopetzky (I.), 1948. Tschermaks Min. Petr. Mitt., ser. 3, vol. 1, p. 69. [M.A. **10**-422.]
Kozik (S.), 1930. Acad. Polonaise Sci. Lett., Cl. Sci. Math. Nat., ser. A, p. 536. [M.A. **5**-285.]
Lacroix (A.), 1922. Min. Madagascar, vol. 2, p. 544. [M.A. **1**-326, **2**-146.]
Larsen (E. S.), 1921. U.S. Geol. Surv. Bull., no. 679, p. 123. [M.A. **1**-367.]
—— and Steiger (G.), 1917. Journ. Washington Acad. Sci., vol. 7, p. 7. [M.A. **1**-206.]
Lyamina (A. N.) and Soboleva (M. V.), 1937. All-Union Sci. Res. Econ. Min., Moscow, no. 110. [M.A. **8**-334.]
Macgregor (A. M.), 1941. Min. Mag., vol. 26, p. 102.
McMurchy (R. C.), 1934. Zeits. Krist., vol. 88, p. 420. [M.A. **6**-45.]
Mélon (J.), 1938. Mém. Acad. Roy. Belg., Cl. Sci., vol. 17, no. 4. [M.A. **7**-360.]
Nockolds (S. R.) and Richey (J. E.), 1939. Amer. Journ. Sci., vol. 237, p. 27. [M.A. **7**-305.]
Norin (R.), 1942. Geol. För. Förh. Stockholm, vol. 64, p. 341. [M.A. **9**-141.]
Orcel (J.), 1927. Bull. Soc. Franç. Min., vol. 50, p. 75. [M.A. **3**-372.]
—— Caillère (S.), and Hénin (S.), 1950. Min. Mag., vol. 29, p. 329.
Osborne (F. F.) and Archambault (M.), 1948. Trans. Roy. Soc. Canada, ser. 3, vol. 42, sect. 4, p. 61. [M.A. **11**-113.]
Pavlovitch (S.), 1931. Bull. Soc. Franç. Min., vol. 53 (for 1930), p. 535. [M.A. **5**-215.]
Pulfrey (W.), 1933. Quart. Journ. Geol. Soc. London, vol. 89, p. 401.
Rondolino (R.), 1936. Periodico Min. Roma, vol. 7, p. 193. [M.A. **6**-505.]
Sanero (E.), 1933. Periodico Min. Roma, vol. 4, p. 473. [M.A. **5**-441.]
Satô (S.), 1933. Journ. Shanghai Sci. Inst., Sect. II, vol. 1, p. 17. [M.A. **5**-527.]
Shannon (E. V.), 1920. Proc. U.S. Nat. Mus., vol. 57, p. 397. [M.A. **1**-171.]
—— 1920. Ibid., vol. 58, p. 371. [M.A. **1**-214.]

Shannon (E. V.) 1923. Amer. Min., vol. 8, p. 8. [M.A. **2**–363.]
—— 1924. Proc. U.S. Nat. Mus., vol. 66, art. 2. [M.A. **3**–204.]
—— 1926. Bull. U.S. Nat. Mus., no. 131, p. 378. [M.A. **3**–130.]
—— and Wherry (E. T.). 1922. Journ. Washington Acad. Sci., vol. 12, p. 239. [M.A. **2**–189.]
Simpson (E. S.), 1936. Journ. Roy. Soc. Western Australia, vol. 22, p. 1. [M.A. **6**–363.]
—— 1937. Ibid., vol. 23, p. 17. [M.A. **7**–114.]
Smith (W. Campbell) with analysis by Prior (G. T.), 1924. Min. Mag., vol. 20, p. 241.
—— Bannister (F. A.), and Hey (M. H.), 1946. Ibid., vol. 27, p. 217.
Sokolov (G. A.), 1931. Trans. Geol. Prosp. Service U.S.S.R., no. 56, p. 3. [M.A. **6**–436.]
Tajder (M.), 1938. Vesnik Geol. Inst. Juguslavije, vol. 6, p. 235. [M.A. **7**–359.]
Tomkeieff (S. I.), 1926. Min. Mag., vol. 21, p. 76.
—— 1943. Irish Nat. Journ. Belfast, vol. 8, p. 67. [M.A. **9**–179.]
Tschermak (G.), 1890. Sitzungsber. Akad. Wiss. Wien, Cl. Mat.-Nat., vol. 99, abt. 1, p. 174.
—— 1891. Ibid., vol. 100, abt. 1, p. 29.
Weiss (A.) and Hofmann (U.), 1951. Zeits. Naturforsch., vol. 6b, p. 405. [M.A. **12**–54.]
Winchell (A. N.), 1926. Amer. Journ. Sci., ser. 5, vol. 11, p. 283. [M.A. **3**–373.]
—— 1936. Amer. Min., vol. 21, p. 642. [M.A. **6**–532.]
Wiseman (J. D. H.), 1934. Quart. Journ. Geol. Soc. London, vol. 90, p. 354. [M.A. **6**–224.]
Wolff (J. E.), 1912. Amer. Journ. Sci., ser. 4, vol. 34, p. 475.
Zepharovich (V. von), 1877. Zeits. Kryst. Min., vol. 1, p. 371.
—— 1878. Ibid., vol. 2, p. 195.

The hydrated calcium silicates riversideite, tobermorite, and plombierite.

By J. D. C. McConnell, M.Sc.
Department of Mineralogy and Petrology, University of Cambridge.

[Communicated by Prof. C. E. Tilley, F.R.S., read March 26, 1953]

Introduction.

In a recent paper Taylor has shown that three distinct hydration levels exist within the 'calcium silicate hydrate (I)' group of artificial preparations (Taylor, 1953*a*, p. 168). The individual hydrates may be distinguished from the position of the 002 reflection in X-ray powder photographs. The *d* spacings corresponding to the three hydrates of this group examined during the present investigation are 14·6, 11·3, and 9·6 Å. These hydrates have $H_2O:SiO_2$ molar ratios of approximately 2·0, 1·0, and 0·5 respectively.

A recent examination of the minerals crestmoreite and riversideite (Taylor, 1953*b*) has shown that both these minerals are intimate intergrowths of members of the above hydrate series with the mineral wilkeite. Both the artificial preparations and the crestmoreite-riversideite intergrowths have failed to provide material suitable for detailed optical study.

During a mineralogical investigation of rocks from a dolerite-chalk contact at Ballycraigy, Larne, County Antrim, a mineral was examined and subsequently identified, from X-ray powder photographs, with the 11·3 Å. hydrate referred to above. Optical and X-ray studies on single crystals of this mineral were made and subsequently both the 14·6 and 9·6 Å. hydrates were prepared from this material experimentally.

X-ray powder photographs of a gelatinous material collected at Ballycraigy showed that this material could also be identified with the 'calcium silicate hydrate (I)' group. A chemical analysis of this substance showed that, in composition, it was closely comparable to the mineral plombierite, a gelatinous material originally described by Daubrée (Daubrée, 1858*b*). That plombierite, as defined by Daubrée, is a gelatinous member of the 'calcium silicate hydrate (I)' group is thought to be highly probable.

Nomenclature.

Precise determination of the optical properties of the individual crystalline hydrates of this group led, inevitably, to the problem of their future nomenclature. In discussing the nomenclature used in the past three facts must be considered:

(1) In the absence of a suitable technique, now provided by X-ray examination, the presence of several hydration states in any hydrate sample could not be readily appreciated. The present investigation has shown that the optical properties of mixed hydrates are mean values.

(2) The instability of the crystalline hydrates of low 002 spacing at normal room-temperature and humidity was not formerly recognized. This instability makes it imperative that specimens of the pure hydrates, once examined, should be stored under conditions which prevent further hydration.

(3) Both crestmoreite and riversideite as described by Eakle (1917) have now been shown to be intimate intergrowths of the hydrate minerals with wilkeite (Taylor, 1953*b*).

As a direct consequence of the fact that no special precautions were taken by Eakle to preserve the riversideite specimens examined by him these now contain only minor amounts of the 9·6 A. hydrate. Thus the high water content of the riversideite specimens examined by Flint (Flint and others, 1938) and Taylor (1953*b*, p. 156) was correctly taken to indicate that the specimens of riversideite examined could be identified with crestmoreite, as defined by Eakle. The conclusion reached by Flint that crestmoreite and riversideite, as defined by Eakle, were identical was, however, invalid on the basis of the present reasoning. Distinctive optical and X-ray characteristics have now been demonstrated for the 9·6 A. hydrate, which is thought to have been the primary hydrate component of the intergrowths described by Eakle as riversideite. Accordingly it is here suggested that the name riversideite be reserved for the 9·6 A. hydrate, should this be found and preserved in an unhydrated state. It should be noted that the chemical composition given by Eakle for riversideite approximates to that of the 9·6 A. hydrate (Eakle, 1917, p. 347).

Claringbull and Hey (1952) have shown, from X-ray powder data, that the mineral tobermorite as described by Heddle (1880) may be identified with the 'calcium silicate hydrate (I)' group of artificial preparations. The 002 reflection recorded by these authors indicates that this mineral is in the 11·3 A. hydration state. Accordingly the mineral name tobermorite will be used in the present account to describe material in

this hydration state. The relative stability of tobermorite from Skye in hydration experiments will be discussed later in the present paper in relation to its alkali content.

Examination of the X-ray powder photographs of the 14·6 Å. hydrate from Ballycraigy, where it results through the hydration of the 11·3 Å. hydrate, shows that its formation is accompanied by a decrease in the number and clarity of the reflections observed. This is associated with a breakdown of the relatively perfect crystal structure of the 11·3 Å. hydrate, and the 002 reflection recorded may be regarded as inherited from the ordered structure of the parent 11·3 Å. hydrate. The natural gels studied correspond in composition to the 14·6 A. hydrate. In the gels crystallization is extremely imperfect and no 002 reflection has been recorded. Consequently the presence or absence of the 002 reflection is thought merely to be indicative of the degree of crystallization. In the event of plombierite being recognized as a member of the 'calcium silicate hydrate (I)' group this mineral name may be adopted to describe the hydrates of the series in which the $H_2O:SiO_2$ molar ratio approximates to 2·0. The present nomenclature is set out in table I.

TABLE I. Distinguishing characters of the calcium silicate hydrates.

	$H_2O:SiO_2$ molar ratio (approximate).	002 spacing.	Refractive indices.
Riversideite . .	0·5	9·6 Å.	α 1·600 β 1·601 γ 1·605
Tobermorite . .	1·0	11·3	α 1·570 β 1·571 γ 1·575
Plombierite . .	2·0	14·6	β 1·550
Gels	variable	absent	variable

THE 11·3 Å. HYDRATE FROM BALLYCRAIGY, LARNE, CO. ANTRIM.

This mineral occurs in cavities in contact-rocks at Ballycraigy. The dolerite-chalk contact from which these rocks were obtained is similar to that at Scawt Hill (Tilley, 1931) and was exposed in a temporary trench. The dolerite intrusion at Ballycraigy, one mile north of Larne, has no connexion with the Scawt Hill plug, six miles north of Larne. The hydrate mineral was found in association with the mineral scawtite in vugs in larnite-rocks from the endogenous zone of the contact, where it occurs as minute radiating aggregates of fibres. In hand-specimens the mineral is characterized by a distinctive silky lustre on cleavage faces and is seen to alter readily to a fine white powder, which

has been identified as the 14·6 Å. hydrate. In some cases the mineral is completely pseudomorphed by calcite. The occasional preservation of the unaltered 11·3 Å. hydrate is ascribed to the compact nature and desiccating action of the enclosing larnite-rocks. The mineral is preserved in the laboratory by storing it over silica gel.

The hydrate dissolves in hydrochloric acid leaving a gelatinous residue of silica, and qualitative microchemical tests indicate abundant calcium. The mineral has a hardness of $2\frac{1}{2}$ and its specific gravity, as determined by suspension, was found to be 2·44.

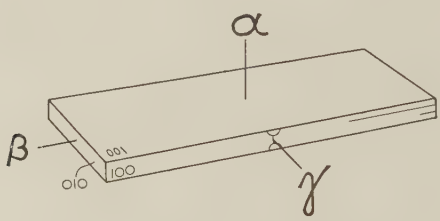


Fig. 1. Optical orientation of the 11·3 Å. hydrate.

In thin section, radiating fibres of the hydrate were found to have positive or negative elongation and straight extinction. The maximum birefringence observed was 0·005. From fibre aggregates in thin section, 2V was found to be small and positive, the optic axial plane lying normal to the length of the fibres. Single crystals of the hydrate were isolated and these were invariably found to be elongated flakes which lay on a perfect cleavage and showed a second cleavage parallel to the length. Crystals in this orientation were found to be negatively elongated. The refractive indices of the hydrate were determined as α 1·570, β 1·571, γ 1·575, all $\pm$0·002. Weak dispersion was noted. The optical orientation of single crystals is illustrated in fig. 1. The crystallographic axes chosen from the single-crystal X-ray study had the following relationship to the optical directions: $a = \gamma$, $b = \beta$, $c = \alpha$. The perfect cleavage is consequently (001) and the second cleavage (100).

Determination of the refractive indices of partly hydrated crystals showed that these were appreciably lower than those given above, which were the values consistently obtained on fresh material. Partial hydration was invariably indicated by the opacity of the hydrated material. The results of a single-crystal X-ray study carried out on carefully selected material are given below (table II).

TABLE II. X-ray powder spacings of the calcium silicate hydrates.

A.		B.		C.		D.	
d.	Int.	*d*.	Int.	*d*.	Int.	*d*.	Int.
11·3	vvs	11·4	vvs	11	s	—	
5·55	vs	5·47	mw	5·6	ms	5·48	w b
3·84	vw	—		—		—	
3·57	ms	3·50	mw	3·55	vvw	—	
3·34	vw	3·34	vw	—		—	
3·24	vw	—		3·28	vvw	3·17 }	ms b
3·11	ms	3·10	s	3·07	vvs	3·01 }	
2·99	ms	2·99	m	2·97	s	—	
2·83	vvs	2·82	ms	2·80	s	2·81	ms
2·75	vw	2·74	vvw	—		—	
2·53	m	2·52	vw	2·52	vw	—	
2·45	mw	2·45	vw	2·48	vw	—	
2·32	ms b	—		—		—	
2·29	m	2·30	w b	2·28	ms	—	
2·15	m	2·15	w	2·15	m	—	
2·10	m	2·09	vw	—		2·07	w
2·01	ms	2·01	mw	2·00	m	—	
—		—		1·93	vvw	—	
1·85	vs	1·847	m	1·83	vs	1·83	ms
—		—		1·81	vvw	—	
1·74	mw	—		1·76	vvw	—	
—		—		1·71	vvw	—	
1·676	ms	1·673	mw	1·67	s	1·67	w
1·627	ms	1·622	vw	1·61	vw	—	
1·570	w	—		1·59	vvw	—	
1·547	w	1·550	w	1·53	m	—	
1·511	vvw	1·503	vvw	—		—	
1·469	vvw	—		—		—	
1·442	vvw	1·442	vw	1·43	vw	—	
1·408	vvw	—		1·405	w	1·403	vw
1·401	vvw	1·402	vvw	1·395	w		
1·381	vvw	1·380	vvw	1·370	vvw		
1·293	vvw	1·290	vvw	—			
1·267	vvw	1·268	vvw	—			
1·261	vvw	1·258	vvw	1·260	vvw		
1·220	vvw	1·220	vvw b	1·225	vw		
1·198	vvw	—		—			
1·181	vvw	1·185	vvw	1·185	vvw		
1·168	vvw	1·170	vvw	1·160	vvw		
1·114	vvw	1·117	vvw b	1·110	w		
1·073	vvw	—		1·075	vw		
1·066	vvw						
1·029	vvw						
0·937	vvw						
0·921	vvw						
0·875	vvw						
0·836	vvw						
0·792	vvw						
0·780	vw						

A. Tobermorite from Ballycraigy, County Antrim.
B. Tobermorite from Tobermory pier, Mull. (Claringbull and Hey, Min. Mag., 1952, vol. 29, p. 961.)
C. Artificial tobermorite. (Sample 58, Taylor, Min. Mag., 1953, vol. 30, p. 158.)
D. Natural 'calcium silicate hydrate (I)' gel (plombierite) from Ballycraigy.

Scale of decreasing intensities: vvs, vs, s, ms, m, mw, w, vw, vvw, vvvw, b = broad from visual estimation.
All photographs taken with Cu-$K\alpha$ radiation and *d* spacings given in Å. units.

Oscillation photographs taken for all three axes confirmed the orthorhombic symmetry of the mineral and indicated the following values for the dimensions of the unit cell: a 11·3, b 7·33, and c 22·6 Å. The space group was found to be $C222_1$ as determined from zero, first, and second layer-line Weissenberg photographs taken about the b-axis. A zero layer-line photograph was also taken on rotation about the a-axis. Reflections with h and k odd were found to be weak and diffuse, and the direction of spread of these spots was found to be along the c^*-axis in reciprocal space, indicating that the mineral is built up of perfect structural slabs normal to c with structural mistakes occurring between these slabs. Since the reflections with h and k odd are extremely weak a smaller pseudo-cell may be defined with $a' = a/2 = 5{\cdot}65$, $b' = b/2 = 3{\cdot}66$, and $c' = c = 22{\cdot}6$ Å. The lattice of the pseudo-cell is body centred and possible space-groups are $Immm$, Imm, $I222$, and $I2_12_12_1$. A list of the d spacings of tobermorite from Ballycraigy is given in table II together with those of tobermorite from Mull and a sample of 'calcium silicate hydrate (I)' prepared by Taylor.

Chemical composition of the 11·3 Å. hydrate from Ballycraigy.

The pure 11·3 Å. hydrate from Ballycraigy has not been analysed. Its composition has, however, been determined indirectly from the analysis of a mixed 11·3–14·6 Å. hydrate. The latter occurs in some abundance in the contact-zone at Ballycraigy, where it has been formed through the hydration of tobermorite. X-ray examination of this material shows that both the 11·3 Å. and 14·6 Å. hydrates are present. In thin sections the mixed hydrate was opaque and the mean of determined refractive indices was 1·550. The following analysis was made by the author on 0·500 gram of material.

Table III. Chemical analysis of a mixed calcium silicate hydrate from Ballycraigy.

		Molar ratio.	$5CaO,6SiO_2,5H_2O$.
SiO_2	44·86	1·00	1·00
CaO	36·02	0·86	0·83
Na_2O	0·05	—	—
K_2O	0·05	—	—
H_2O+	11·10	0·82	0·83
H_2O-	8·32	—	—
	100·40		

The analysis (table III) shows that the mixed hydrate is essentially a pure hydrated calcium silicate. Assuming that the loss of water at 105° C. corresponds to the dehydration of all the material present to the

11·3 Å. hydration state the molar ratios given in the second column above correspond to the 11·3 Å. hydrate. From the density and cell dimensions already given the contents of the pseudo-cell may be written: $5CaO.6SiO_2.5H_2O$. The cumulative dehydration curve given in a later section suggests that part of the water present in the 11·3 A. hydrate occurs as hydroxyl groups. The above formula may then be written $(OH)_2CaCa_4Si_6O_{16}.4H_2O$. In this formula an attempt has been made to satisfy the symmetry of the pseudo-cell.

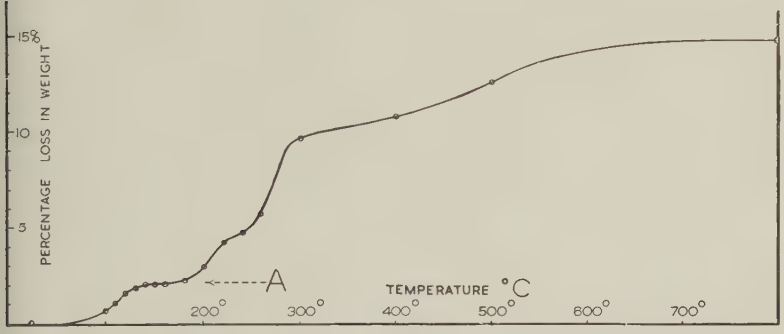


Fig. 2. Cumulative dehydration curve drawn for the 11·3 Å. hydrate.

Preparation of the 9·6 Å. and 14·6 Å. hydrates.

The cumulative dehydration curve shown in fig. 2 was prepared from data obtained on a very small quantity of the 11·3 A. hydrate from Ballycraigy. The initial loss of part of the water present in the sample was thought to indicate that a small quantity of the 14·6 A. hydrate was present. On this assumption the level, marked A on the diagram, was thought to correspond to the 11·3 A. hydrate. The dehydration curve also shows a marked point of inflexion below 300° C. corresponding to the formation of the 9·6 A. hydrate. Dehydration was considered complete at a temperature of 800° C. A similar dehydration curve for natural intergrowths of the hydrate minerals with wilkeite has been given by Taylor (1953*a*, p. 165).

Examination of powder photographs of the 11·3 A. hydrate held at 300° C. for a short time showed that the 002 spacing had been reduced to 9·6 A. Single crystals of the 9·6 A. hydrate thus produced were examined optically. The optical orientation of the single crystals was found to be unchanged, but a general increase in the refractive indices was recorded. These were α 1·600, β 1·601, γ 1·605, all $\pm$0·002, and

increased dispersion was noted. The *d* spacings of the artificial 9·6 Å. hydrate are given in table IV below.

TABLE IV. X-ray powder spacings of the 9·6 Å. hydrate.

d.	Int.	*d*.	Int.
9·67	s	2·10	vw
4·83	s	2·02	vw
3·62	w	1·834	w
3·16	ms	1·659	w
3·04	vs	1·526	w
2·79	ms	1·393	vvw
2·35	ms	1·106	vvw
2·17	vw	1·067	vvw

As already noted, the 11·3 Å. hydrate alters readily to the 14·6 Å. hydrate when exposed to the atmosphere. A direct attempt to demonstrate this hydration process in the laboratory was made as follows. A small quantity of the 11·3 Å. hydrate, in which scawtite was present as an impurity, was photographed on a low-angle focusing X-ray camera. The resulting photograph showed a strong but diffuse 002 reflection corresponding to a *d* spacing of 12·0 A. This was taken to indicate that the 11·3 Å. hydrate was partly hydrated. The material on the camera was subsequently moistened with water and re-photographed. Two very sharply defined reflections were recorded. The first of these which was very strong corresponded to a *d* spacing of 14·6 Å. The second was a very faint reflection and corresponded to a *d* spacing of 11·3 Å. The presence of the latter reflection was taken to indicate that the cores of some of the larger crystals present remained unhydrated. An account of a similar hydration experiment on the mineral tobermorite from Skye is given in the following section.

Comparison of tobermorite from Skye with that from Ballycraigy.

X-ray powder data for tobermorite from Mull and tobermorite from Ballycraigy are compared in table II. A specimen of tobermorite from Loch Eynort in Skye supplied by the British Museum (specimen number B.M. 1952,35) was examined by the present author. Optical examination confirmed the data already given for this mineral by Claringbull and Hey (1952, p. 962). The birefringence of the minute crystals present was found to be 0·005 approximately, and the limits of refringence were 1·545 and 1·565. Claringbull and Hey noted that the refractive indices of this material varied with its opacity. Increase in opacity is now correlated

with decrease in the mean refractive index, a condition already noted in examination of tobermorite from Ballycraigy. Accordingly, it is suggested that the Loch Eynort material is not perfectly homogeneous in respect of its water content.

Attempts were made, in the manner outlined in the previous section, to alter the strong 11·3 A. spacing of tobermorite from Skye by further hydration. The strong 11·3 A. reflection given by this material was unaltered even after it had been ground up with water. The significance of the stability of tobermorite from Skye will be discussed in a later section in relation to the alkali content of this mineral and to the interlayer structure of the hydrates.

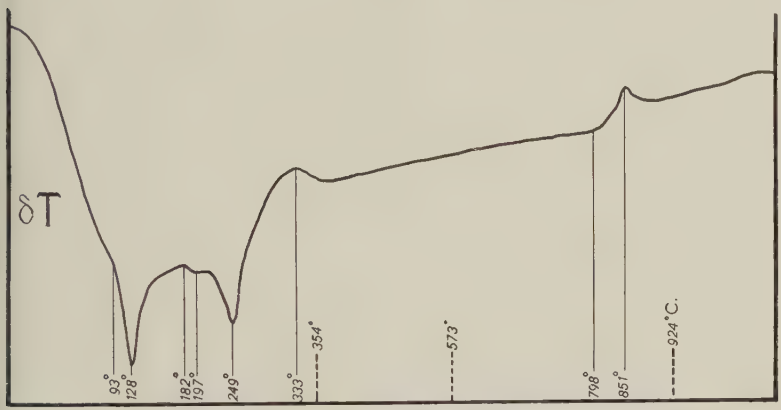


Fig. 3. Differential thermal curve of an 11·3–14·6 Å. hydrate mixture from Ballycraigy, Co. Antrim.

Differential thermal analysis of the 11·3–14·6 Å. hydrate mixture.

The chemical composition of this mixed hydrate has already been given in the section on the composition of the 11·3 Å. hydrate. A differential thermal analysis of the mixed hydrate was carried out by Dr. R. J. W. McLaughlin of the Department of Mineralogy and Petrology, Cambridge. The resulting differential thermal curve is shown in fig. 3. The most important features of this curve are the marked endothermic peaks at 128° and 249° C. Exothermic reactions are indicated by peaks at 333° and 851° C. The last was shown to correspond to the formation of $CaSiO_3$ by taking a powder photograph of material held at a temperature in excess of 900° C. for a short period.

Comment will be made in a later section of the present paper on the close similarity which exists between the above differential thermal analysis curve and that of Ca-substituted vermiculite. In the same section the relationship between the interlayer structure of the hydrates studied and the vermiculite minerals will be discussed.

A natural gelatinous member of the 'calcium silicate hydrate (I)' group.

X-ray powder data for a gelatinous material found at Ballycraigy are given in table II. This material has been identified with the 'calcium silicate hydrate (I)' group from the reflections observed in powder photographs. These compare closely with those of a poorly crystalline artificial hydrate prepared at room-temperature by Taylor. The composition of the latter sample, which was prepared from $Ca(OH)_2$ and SiO_2 gel, was $1{\cdot}3CaO:SiO_2:2{\cdot}1H_2O$.

In thin section the gelatinous material from Ballycraigy is seen to replace both larnite and bredigite and has a low birefringence thought to be due to the partial orientation of the crystallites present. In the pseudomorphs after larnite the delicate twinning of the latter mineral is preserved.

In attempting to identify the natural gel with some known mineral its composition was compared with that given for the mineral plombierite, described originally by Daubrée (1858). Analyses of plombierite and the natural gel are compared below.

Table V. Chemical analyses of plombierite and the Ballycraigy gel.

	A.	B.
SiO_2	40·6	40·4
CaO	34·1	32·6
Al_2O_3	1·3	2·4
Fe_2O_3	—	0·8
MgO	—	0·3
H_2O	23·2	23·3
	99·2	99·8

A. Plombierite, Plombières, Vosges, France. (G. A. Daubrée, 1858*b*, p. 245.)

B. Analysis, on 0.200 gm., of the natural gel from Ballycraigy, County Antrim, by the author. Iron present was determined as Fe_2O_3. The alkali content was not determined.

Comparison of the chemical analyses given above together with Daubrée's comments on the gelatinous character of plombierite suggest that plombierite and the gel from Ballycraigy are identical. Confirmation of the identity postulated may eventually be provided by X-ray powder photographs of Daubrée's material which is at present unavailable.

Considerable experimental work has been done on the gelatinous members of the 'calcium silicate hydrate (I)' group and methods of preparation have been listed by Taylor (1950, p. 3689). These include the hydration of tricalcium silicate. The artificial gels are characterized by variable $CaO:SiO_2$ molar ratio, and the general formula indicated by Bessey (1938, p. 209) is $1–1{\cdot}5CaO.SiO_2.n–xH_2O$. The chemical composition of the natural gel from Ballycraigy indicates that the lower limit of the $CaO:SiO_2$ molar ratio in the above formula may be reduced to 0·85 approximately.

A more detailed account of the optical and physical properties of the natural gels will be given in a later paper. Further study of the natural gels is justified by the fact that the formation of similar material is thought to be a primary factor producing 'set' in portland cement hydrated at room-temperature.

General conclusions on the interlayer structure of the hydrates.

Taylor has suggested (1953*a*, p. 169) that the water present in the hydrates in excess of one molecule is loosely held between the primary structural sheets, and an analogy with the clay minerals is postulated. The present investigation indicates that a close analogy exists between the hydrate minerals and vermiculite, in the same connexion. In vermiculite the normal 002 spacing is 14 A. Loss of part of the interlayer water at 110° C. reduces this spacing to 11·8 A. and the spacing is further reduced to 9·3 A. on the loss of the remaining water at still higher temperature. These two water fractions are described as 'unbound' and 'bound' water respectively (Walker, 1951, p. 206). Differential thermal analysis curves for normal vermiculite show two strong endothermic peaks at low temperature corresponding to the loss of these water fractions (Barshad, 1948, p. 664). Current theory suggests that Mg ions are present in the interlayer zones in normal vermiculite and that these are surrounded by hydration shells of water molecules. Part of the water present is in an 'unbound' condition and is liberated from the interlayer zone at a temperature of 110° C. (Walker, 1951, p. 206).

Recent work by Barshad (1948) has shown that the Mg ions in interlayer positions in vermiculite may be replaced by other cations and that the cation substituted controls the character of the differential thermal analysis curve and the 002 spacing of the substituted vermiculite in different hydration states. Examination of the effects of Ca-substitution on the 002 spacing and the differential thermal analysis curve is of

interest in the present discussion. At normal temperature the 002 spacing of Ca-substituted vermiculite is 15·07 Å. On complete dehydration this spacing is reduced to 9·55 Å. As in normal Mg-vermiculite two endothermic peaks are present in the differential thermal analysis curve of Ca-vermiculite indicating the presence of 'unbound' and 'bound' water fractions. These peaks occur at slightly lower temperature than the corresponding peaks for Mg-vermiculite. In Na-substituted vermiculite only one endothermic peak is recorded, and the 002 spacing of air-dried material is 12·5 Å.

A close analogy between the interlayer structure of the hydrates at present studied and that of the vermiculite minerals is indicated by:

(1) The close similarity between the 002 spacings of the hydrates and the hydration states of Ca-vermiculite.

(2) The close similarity between the differential thermal analysis curve of the mixed 11·3–14·6 Å. hydrate from Ballycraigy and that of Ca-vermiculite.

The above comparisons suggest that Ca ions are present in the interlayer zones of the hydrate minerals from Ballycraigy. The persistence of the 11·3 Å. spacing in the mineral tobermorite from Skye is explained as being due to the presence of alkali ions in the interlayer positions. It is proposed to test the validity of the above hypothesis by cationic exchange experiments on the hydrate minerals.

Acknowledgements.—The author wishes to thank Dr. A. M. B. Douglas, of the Department of Mineralogy and Petrology, Cambridge, for interpreting the Weissenberg photographs taken during the present investigation, and Dr. R. J. W. McLaughlin of the same department, who carried out the differential thermal analysis. The X-ray photographs were taken by Mr. Kenneth Rickson. To Dr. H. F. W. Taylor and to the Trustees of the British Museum thanks are due for the loan of material.

This research was carried out in the Department of Mineralogy and Petrology, Cambridge, under the direction of Professor C. E. Tilley, for whose advice and encouragement the author is most grateful. The author at present holds a Research Grant from the Ministry of Education for Northern Ireland.

References.

Barshad (I.), 1948. Vermiculite and its relation to biotite as revealed by base exchange reactions, X-ray analyses, differential thermal curves, and water content. Amer. Min., vol. 33, pp. 655–78. [M.A. **10**–462.]

Bessey (G. E.), 1938. The calcium aluminate and silicate hydrates. Symposium on the chemistry of cements. Stockholm, 1938, pp. 178–215.

Claringbull (G. F.) and Hey (M. H.), 1952. A re-examination of tobermorite. Min. Mag., vol. 29, pp. 960–962.

Daubrée (G. A.), 1858*a*. Mémoire sur les dépôts minéraux formés par les sources thermales de Plombières, avant et pendant la période actuelle. Première partie. Formation contemporaine des zéolithes. Compt. Rend. Acad. Sci. Paris, vol. 46, pp. 1086–1090.

— 1858*b*. Sur la relation des sources thermales de Plombières avec les filons métallifères et sur la formation contemporaine des zéolithes. Annales des Mines, ser. 5, vol. 13, pp. 227–256.

Eakle (A. S.), 1917. Minerals associated with the crystalline limestone at Crestmore, Riverside County, California. Bull. Dept. Geol. Univ. California, vol. 10, no. 19, pp. 327–360.

Flint (E. P.), McMurdie (H. F.), and Wells (L. S.), 1938. Formation of hydrated calcium silicates at elevated temperatures and pressures. Journ. Res. Nat. Bur. Standards U.S.A., vol. 21, pp. 617–638. [M.A. **7**–283.]

Heddle (M. F.), 1880. Preliminary notice of substances which may prove to be new minerals. Min. Mag., vol. 4, pp. 117–123.

Taylor (H. F. W.), 1950. Hydrated calcium silicates, Part I. Compound formation at ordinary temperatures. Journ. Chem. Soc. London, pp. 3682–3690. [M.A. **11**–314.]

—— 1953*a*. Hydrated calcium silicates Part V. The water content of calcium silicate hydrate (I). Ibid., pp. 163–171. [M.A. **12**–172.]

—— 1953*b*. Crestmoreite and riversideite. Min. Mag., vol. 30, pp. 155–165.

Tilley (C. E.), 1931. The dolerite-chalk contact of Scawt Hill, Co. Antrim. The production of basic alkali-rocks by the assimilation of limestone by basaltic magma. Min. Mag., vol. 22, pp. 439–468.

Walker (G. F.), 1951. Vermiculites and some related mixed-layer minerals. X-ray identification and crystal structures of clay minerals. Min. Soc. London, pp. 199–223.

The identification and determination of plagioclase felspars by the X-ray powder method.

By J. Goodyear, Ph.D., A.Inst.P., and W. J. Duffin, M.A., A.Inst.P.
Physics Department, University College, Hull.

[Read November 5, 1953.]

1. Introduction.

THERE appear to be few published data correlating X-ray powder patterns of chemically analysed plagioclase felspars with composition. Tuttle and Bowen (1950) have examined the powder patterns of low-temperature and high-temperature modifications and find that pure albite from Amelia, Virginia, when heated for ten days at 1050° C., gives a powder pattern identical with that of synthetic albite. They have not given, however, complete data over the whole range from Au_0Ab_{100} to $An_{100}Ab_0$. Claisse (1950) selected six reflections from the powder patterns of eight plagioclases of composition extending over the complete range, and plotted line separations against composition determined optically, but did not distinguish between high- or low-temperature forms.

More recently, Gay (1953) has examined the single-crystal diffraction patterns of a number of plagioclases in the range $An_{70}Ab_{30}$–$An_{100}Ab_0$, and has correlated the nature of each pattern with the composition and thermal history of the specimen. Gay's work has provided a convenient method for distinguishing between high- and low- temperature forms of anorthite: he has found that pure anorthites which have been heated naturally give the same type of pattern as a synthetic anorthite crystallized at a temperature of the order of 1500° C.; further, when this synthetic anorthite is 'annealed' at 1100° C. for 72 hours the pattern obtained is of the type given by pure anorthites of low-temperature origin.

In the present work are examined powder patterns of chemically analysed plagioclases of presumably low-temperature origin, and of synthetic materials probably having high-temperature structures. The aim of this paper is twofold: (i) to provide X-ray powder data for the identification of plagioclase felspars when admixed with associated

minerals, and (ii) to establish relationships enabling the composition and thermal modification of a felspar to be determined from certain line positions in the X-ray pattern.

2. Description of the plagioclase specimens.

Descriptions of the materials employed in this investigation are given in tables I and II. The specimens were supplied to the authors by Dr. W. H. Taylor, but had been presented to him by the following:

Prof. C. E. Tilley, Department of Mineralogy and Petrology, University of Cambridge.
Prof. R. C. Emmons, University of Wisconsin.
Prof. H. H. Hess, University of Princeton, New Jersey.
Prof. T. G. Sahama, Institute of Geology, Helsinki, Finland.
Prof. H. Kuno, Geological Institute, Tokyo University, Japan.

Table I. Details of natural plagioclases

Specimen no.	Source.	Ref.	Name and locality.	Mode of occurrence.	Composition (wt. %) from Chem. anal. Ab.	An.	Or.	R.I. An.
1.	Emmons	A (31)	Albite, Rutherford mica mine, Amelia, Va.	Pegmatite	98·0	0·4	1·6	0·0
2.	Emmons	A (4)	Oligoclase, Petrick quarry, Llano Co., Texas.	Granite	81·6	16·5	1·9	19·2
3.	Sahama	B (9)	Oligoclase, Hawk mica mine, N.C.	Crystals from pegmatite	74·4	22·1	3·5	20·8
4.	Emmons	A (28)	Andesine, Corundum Hill mine, Macon Co., N.C.	See ref. A (28)	68·2	31·1	0·7	27·4
5.	Emmons	A (8)	Andesine, Crestmore, Calif.	Granodiorite	60·2	38·0	2·0	34·8
6.	Emmons	A (10)	Labradorite, Shelby, N.C.	Hornblende-gabbro	47·3	51·6	1·1	46·5
7.	Emmons	A (17)	Labradorite, Grand Marais, Minnesota.	Anorthosite	32·7	64·5	2·8	62·0
8.	Emmons	A (18)	Labradorite, Chester Co., Pennsylvania.	Diabase	31·6	66·3	2·1	
9.	Emmons	—	Bytownite, Crystal Bay, Minnesota.	Anorthosite	28·7	71·3	0·0	—
10.	Hess	B (4)	Bytownite, Rustenburg mines, Transvaal.	Norite	22·0	77·0	1·0	73·6
11.	Hess	B (3)	Bytownite, Stillwater, Montana.	Anorthosite	18·6	81·0	0·4	78·1
12.	Emmons	A (27)	Bytownite, Merrill, Wis.	Troctolite	16·7	81·5	1·8	77·9
13.	Hess	B (2)	Bytownite, Stillwater, Montana.	Anorthosite	13·2	86·5	0·3	85·0
14.	Tilley	B (1)	Anorthite, Grass Valley, California.	Olivine-norite	6·7	93·0	0·3	93·6
15.	Kuno	—	Anorthite, Hakoné volcano, Japan.	Allivalite, ejected block in volcanic tuff	1·4	98·3	0·3	—
16.	Tilley	—	Anorthite, Pasmeda Alp, Fassa Valley, Tirol.	Veins in limestone block	—	—	—	~100

References: A, Emmons (1953); B, Kracek and Neuvonen (1952).

TABLE II. Details of synthetic plagioclases.*

Specimen no.	Crystallization temperature.	Composition, wt. % An.
17	1090° C.	5
18	1090	10
19	1140	30
20	1160	40
21	1265	60
22	1310	70
23	1350	80
24	1385	90
25	1400	100
26	1520	100

* All these materials came from Dr. J. F. Schairer originally, but were obtained (along with specimens of natural materials) from the collections in the Department of Mineralogy and Petrology and in the Crystallographic Laboratory of the University of Cambridge.

Specimens 17 to 26 were synthesized by Dr. J. F. Schairer, Geophysical Laboratory, Washington, D.C., and obtained by Prof. Tilley.

The compositions have been determined from the chemical analyses on the basis of relative amounts of Na_2O, CaO, and K_2O, without any attempt to eliminate excess silica; compositions have also been calculated from refractive indices using the equations of Chayes (1952). Full chemical analyses and values of refractive indices appear in the references appended to table I. In the case of Emmons's specimens the composition obtained from refractive index measurements represents an average from determinations on three to six grains, the composition of the grains for any specimen differing by as much as 8 % anorthite. Since in no case is the orthoclase content excessive, a consideration of its effect on the X-ray data has been ignored.

All the synthetic materials with the exception of specimen 26 (100 % anorthite) crystallized in a finely divided form, sufficient to give continuous X-ray powder reflections. Specimen 26, however, was prepared at a later date and has been examined by Gay (1953) using a single-crystal technique.

Specimen 15 is of volcanic origin and is likely to be a high-temperature material, whilst the remaining natural specimens are probably low-temperature forms. The complete powder pattern of the former is not considered in this paper.

3. THE X-RAY DATA.

It is well known that the composition of a felspar can vary considerably throughout a particular specimen; this is well illustrated by the

spread of values that can occur when an attempt is made to determine the composition of the material by studying the optics of several grains. If X-ray diffraction patterns are to be linked with bulk chemical analyses, the specimen to be X-rayed should contain a representative selection of material, a condition that can be fulfilled by the powder method.

X-ray diffraction photographs were taken with filtered Co-$K\alpha$ radiation, using a 20 cm.-diameter semi-focusing camera of the type employed by Brindley and his co-workers (1946). In the experimental arrangement the powder is packed, without adhesive, in a shallow cavity ($4 \times 3 \times 0{\cdot}5$ mm.) in a flat glass plate. By varying the angle between the flat specimen surface and the incident beam, focusing in different regions of Bragg angle can be achieved. To eliminate systematic errors in calibration, the powder pattern of rock-salt was recorded on each felspar photograph; this method proved quite satisfactory as only a few calibration lines were added to the complicated felspar patterns. With this technique the position of a good quality reflection was reproducible to within 0·01° in θ. A few photographs have also been taken using an evacuable 19 cm. camera of the Bradley type. Although these had the advantage of low background, nevertheless the resolution was not sufficiently good for reflections occurring close together.

In tables III and IV are listed the powder patterns of natural and synthetic plagioclases. Reflections of spacing greater than about 2·5 kX have been measured and relative intensities estimated visually. For identification purposes, the patterns become too complex below 2·5 kX, but there is a useful characteristic group of three reflections in the range 1·76–1·84 kX. The latter are described as 4, 5, and 6 by Claisse (1950), and will be described in section 5.

Lattice spacings have been calculated for natural materials of compositions 0, 55, and 100 % anorthite using the parameters given by Cole, Sörum, and Taylor (1951), and for synthetic albite using data given by Donnay and Donnay (1952). It seems that, in general, all the observed patterns can be accounted for in terms of reflections for which $(h + k)$ is even, the indices referring in all cases to a c-axis $\sim$7 kX. These constitute the (a)-type reflections described by Gay (1953), and it is probable that Gay's (b)-, (c)-, and (d)-type reflections are not observed with the present technique (but see section 4e).

Certain reflections have been omitted from the pattern of specimen 2 since they were identified as quartz lines, and indeed the chemical analysis of this material indicated the presence of about 19 % free

TABLE III. X-ray powder patterns of

Albite 0 % An. (calc.)		1 Albite 0·4 % An.		2 Oligoclase 16·5 % An.		4 Andesine 31·1 % An.		5 Andesine 38·0 % An.		6 Labradorite 51·6 % An.		Labradorite 55 % An. (calc.)	
hkl.	*d* (kX).	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*hkl.*	*d* (kX).
—	—	—	—	—	—	—	—	—		6·43	w	$1\bar{1}0$	6·42
001	6·38	6·38	m	6·37	m	6·40	wm	6·40	wm	—	—	—	—
020	6·36	—	—	—	—	—	—	—	—	—	—	020	6·40
—	—	—	—	—	—	—	—	—	—	—	—	001	6·35
—	—	—	—	—	—	—	—	—	—	—	—	—	—
$1\bar{1}0$	6·29	—	—	—	—	—	—	—	—	—	—	—	—
$11\bar{1}$	5·89	5·93	w	5·92	f	5·86	f	5·85	f	—	—	$11\bar{1}$	5·82
$\bar{1}11$	5·57	5·60	w	5·61	f	5·63	f	5·65	f	—	—	$\bar{1}11$	5·61
$0\bar{2}1$	4·65	—	—	—	—	4·68	f	4·67	f	4·67	f	$0\bar{2}1$	4·67
$20\bar{1}$	4·018	4·016	s	4·018	s	4·024	s	4·028	s	4·026	s	$20\bar{1}$	4·028
$1\bar{1}1$	3·847	3·843	wm	3·851	wm	3·863	wm	3·870	wm	3·878	wm	$1\bar{1}1$	3·881
—	—	—	—	—	—	—	—	—	—	—	—	—	—
111	3·771	3·767	ms	3·754	ms	3·745	ms	3·751	ms	3·749	ms	111	3·758
—	—	—	—	3·678	m	3·708	ms	3·715	m	3·723	ms	$1\bar{3}0$	3·729
130	3·676	—	—	—	—	—	—	—	—	—	—	130	3·645
131	3·658	3·660	s b	3·651	m	3·634	ms	3·640	ms	3·633	ms	$13\bar{1}$	3·624
$1\bar{3}0$	3·651	—	—	—	—	—	—	—	—	—	—	—	—
$11\bar{2}$	3·496	3·495	m	3·481	wm	3·469	wm	3·468	wm	3·464	wm	112	3·463
$22\bar{1}$	3·473	—	—	—	—	3·421	vw	3·430	vw	3·424	vw	$22\bar{1}$	3·431
$\bar{1}12$	3·371	3·364	wm	3·355	wm	3·356	m	3·359	m	3·352	m	$\bar{1}12$	3·354
—		—			—	—	—	—		—	—	—	—
—	—	—			—	—	—	—	—	—		220	3·212
$20\bar{2}$	3·206	3·206	s	3·198	s	—	—	—	—	—	—	—	—
002	3·188	—	—	—	—	—	—	—	—	—	—	—	—
040	3·182	3·179	vvs	3·176	vvs	3·195	vvs	3·199	vvs	3·197	vvs	040	3·201
—	—	—	—	—	—	—	—	—	—	—	—	$20\bar{2}$	3·192
—	—	—	—	—	—	3·166	s	3·169	vs	3·165	vs	002	3·173
220	3·165	—	—	—	—	3·132	ms	3·134	ms	3·131	ms	220	3·140
$2\bar{2}0$	3·144	3·141	wm	3·142	wm					—	—	—	—
$1\bar{3}1$	2·959	2·952	ms	2·975	m	2·993	m	2·999	m	3·003	m	$1\bar{3}1$	3·005
$22\bar{2}$	2·947		—			—	—	—	—	—	—	—	—
022	2·924		—			—	—	—	—	—	—	—	—
$04\bar{1}$	2·921	2·919	m	2·927	ms	2·929	ms b	2·928	ms b	2·933	ms	$04\bar{1}$	2·939
—						—	—		—	2·916	wm	$0\bar{2}2$	2·923
—						—	—	—	—			222	2·909
131	2·858	2·856	m	2·837	m	2·829	m	2·833	m	2·834	m	131	2·839
—	—	—	—	—	—	—	—	—	—	—	—	$3\bar{1}1$	2·653
$31\bar{1}$	2·658	—	—	—	—	—	—	—	—	—	—	$31\bar{1}$	2·652
$\bar{1}32$	2·633	2·638	wm	2·642	wm	2·646	wm	2·647	wm	2·648	m	$\bar{1}32$	2·643
				—		—	—	—	—	—	—	—	—
				—		—		—		—		221	2·529
$\bar{3}11$	2·620					—		—			—		—
									—	—	—	—	—
					—		—			—		—	
$24\bar{1}$	2·555	2·561	m	2·545	m	2·529	m	2·528	ms	2·525	ms	$24\bar{1}$	2·523
$31\bar{2}$	2·522	—	—	—	—	—	—	—	—	—	—	$31\bar{2}$	2·515
$1\bar{1}2$	2·508	2·509	vw	2·511	vw	2·515	vw	—	—	—	—	$1\bar{1}2$	2·515
$2\bar{2}1$	2·491	—		—	—		—	—		—	—	—	—
$\bar{3}12$	2·474	—			—	—		—	—	—	—	$\bar{3}12$	2·489
—		—			—	—			—	—	—	—	—
$\bar{2}41$	2·443	2·443	wm	2·465	wm	2·487	wm	2·489	m	2·494	m	$\bar{2}41$	2·489

Scale of intensities: vvs very very strong (10), s strong (8), m medium (6), or weak (4), f faint (2); b broad line or two unresolved lines, ? exceptionally spotty, * masked by calibration reflection of rock-salt.

ome natural plagioclase felspars.

7 Labradorite 64·5 % An.		9 Bytownite 71·3 % An.		10 Bytownite 77·0 % An.		12 Bytownite 81·5 % An.		14 Anorthite 93·0 % An.		Anorthite 100 % An. (calc.).	
d (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*hkl.*	*d* (kX).
6·47	w	6·50	w	6·51	w	6·52	w	6·55	w	$1\bar{1}0$	6·51
—	—	.		—	—					—	—
—	—	. .		.	—					020	6·41
		.		.	—			.		001	6·35
		.		—	—				.		—
—					—			—	—	111	5·77
—	—			—	—	—		—	—	$\bar{1}11$	5·64
4·67	w	4·69	wm	4·68	wm	4·68	wm	4·69	m	$02\bar{1}$	4·67
4·036	s	4·025	s	4·024	s	4·021	s	4·033	ms	$20\bar{1}$	4·030
3·885	wm	3·887	wm	3·880	wm	3·885	wm	3·911	wm	$1\bar{1}1$	3·908
	—			—	—	.	.	3·770	ms	130	3·775
3·747	s	3·745	s	3·740	s	3·743	s	3·740	wm	111	3·749
.	—	. .		—			—				—
—	—	—		—		—	—			130	3·613
3·631	ms	3·615	ms	3·617	ms	3·609	ms	3·611	ms	$13\bar{1}$	3·596
—		—		—			—	—	—	—	—
3·463	wm	3·454	wm	3·452	wm	3·456	wm	3·452	wm	$11\bar{2}$	3·452
3·423	vw	3·401	w	3·404	w	3·404	vw	3·390	vw	$22\bar{1}$	3·396
3·359	m	3·346	m	3·350	m	3·347	m	3·354	m	112	3·356
3·254	wm?	3·245	wm?	3·250	wm?	—	—	—	—	—	—
3·222	s	3·222	m	3·222	wm	3·231	ms	3·249	s	$2\bar{2}0$	3·254
—	.	—		. .	—	—	—	.			.
—	—	—		—	.	.	—			—	—
3·198	vvs	3·191	vvs	3·190	vvs	3·191	vvs	3·197	vvs	040	3·204
—	—	—	.		.	—	.		—	$20\bar{2}$	3·188
3·170	vs	3·161	s	3·159	s	3·160	s	3·164	s	002	3·173
3·131	ms	3·117	ms	3·116	m	3·115	ms	3·114	ms	220	3·116
—							—				—
3·013	wm	3·015	wm	3·011	wm	3·016	m	3·030	m	$13\bar{1}$	3·036
—	.				—	—	.			—	.
—	—					—		.		—	—
2·940	ms b	2·937	ms b	2·939	ms b	2·933	ms b	2·944	ms	$04\bar{1}$	2·946
	—	—	—	2·916	wm	—	—	2·927	wm	022	2·928
—		—			—	2·887	vw	2·880	wm	222	2·887
*	m	*	m	*	m	*	m	*	m	131	2·822
—	.	—	—				—	.		$3\bar{1}1$	2·670
—		—	—		—		.	—	—		—
2·651	m	2·642	m	2·647	m	2·652	m	2·649	m	$\bar{1}32$	2·650
—	—	—	—		.	—	—	—		$31\bar{1}$	2·642
—	—	—	—	—	—	—	—	—	—	$2\bar{2}1$	2·554
—	—	—	—			—	—				—
—	.	—				—	—		.	$1\bar{1}2$	2·524
—	—	—			—	—	—	2·519	ms	$\bar{2}41$	2·520
2·522	ms	2·506	s	2·511	ms	2·513	ms	—	—	—	—
—	—	—	—	—	—	—	—	—	—	$31\bar{2}$	2·504
—	—	.	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	—	—
—	—	—	—	—	—	—	—	—	—	$\bar{3}12$	2·499
—	—	—	—	—	—	—	—	2·497	ms	$24\bar{1}$	2·496
2·504	m	—	—	.	—	—	—	—	—	—	—

TABLE IV. X-ray powder patterns o

High-albite (calc.).		17 5 % An.		18 10 % An.		19 30 % An.		20 40 % An.	
hkl.	d (kX).	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.
$1\bar{1}0$	6·44	—	—	—	—	—	—	—	—
020	6·41	6·42	m	6·43	m	6·42	wm	6·47	wm
001	6·35	—	—	—	—	—	—	—	—
$11\bar{1}$	5·83	5·85	w	5·85	w	—	tr	—	—
$\bar{1}11$	5·64	5·64	w	5·66	w	—	tr	—	—
$0\bar{2}1$	4·68	4·69	vw	4·68	vw	4·68	m	4·67	wm
$20\bar{1}$	4·036	4·019	s	4·022	s	4·015	s	4·015	s
$1\bar{1}1$	3·881	3·866	wm	3·872	wm	3·871	wm	3·883	wm
$1\bar{3}0$	3·747	3·732	s	3·735	s	3·734	s	3·739	ms
111	3·740	—	—	—	—	3·673	vw	3·687	w
130	3·636	3·621	ms	3·623	ms	3·620	ms	3·621	m
$13\bar{1}$	3·628	—	—	—	—	—	—	—	—
$\bar{1}31$	3·489	—	—	—	—	—	—	—	—
$11\bar{2}$	3·476	3·457	w	3·463	w	3·458	w	3·458	wm
$22\bar{1}$	3·426	3·411	f	3·420	vw	3·405	vw	3·409	vw
$\bar{2}21$	3·405	—	—	—	—	—	—	—	—
$\bar{1}12$	3·364	3·354	m	3·357	m	3·352	m	3·360	m
$2\bar{2}0$	3·221	—	—	3·249	vw	3·250	vw	3·253	m
$20\bar{2}$	3·207	—	—	—	—	—	—	—	—
040	3·206	3·198	vvs	3·201	vvs	3·196	vvs	3·199	vvs
002	3·174	3·160	s	3·163	s	3·162	s	3·174	vs
220	3·124	3·115	ms	3·119	ms	3·118	ms	3·119	ms
$1\bar{3}1$	3·016	3·003	m	3·006	m	3·007	m	3·012	m
$04\bar{1}$	2·949	2·936	ms	2·941	ms	2·933	ms	2·932	ms b
$0\bar{2}2$	2·930	—	—	—	—	—	—	—	—
$22\bar{2}$	2·919	2·908	m	*	—	2·905	m	*	—
131	2·828	—	—	—	—	—	—	—	—
$\bar{1}32$	2·650	2·646	wm	2·646	wm	2·648	wm	2·648	wm
$31\bar{1}$	2·650	—	—	—	—	—	—	—	—
$2\bar{2}1$	2·532	—	—	—	—	—	—	—	—
$31\bar{2}$	2·523	—	—	—	—	—	—	—	—
$24\bar{1}$	2·521	—	—	—	—	—	—	—	—
$1\bar{1}2$	2·515	2·510	ms	2·508	ms	2·511	ms	2·509	ms
$\bar{2}41$	2·504	—	—	—	—	—	—	—	—

Scale of intensities: vvs very very strong (10), s strong (8), m medium (6) w weak (4), f faint (2), tr trace (not recorded); b broad line or two unresolved lines ? exceptionally spotty, * masked by calibration reflection of rock-salt.

ome synthetic plagioclase felspars

21		22		23		24		25	
60 % An.		70 % An.		80 % An.		90 % An.		100 % An.	
d (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.	*d* (kX).	Int.
—	—	—	—					—	—
6·48	wm	6·53	w	6·51	w	6·54	vw	6·48	vw
—	—	—	—			—	—		—
—	—	—	—		—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
4·67	wm	4·69	wm	4·69	wm	4·69	m	4·70	m
4·021	s	4·026	s	4·015	s	4·032	s	4·039	s
3·892	wm	3·892	m	3·888	wm	3·913	wm	3·923	wm
3·746	s	3·747	s	3·743	s	3·763	s	3·774	s
3·678	w	3·672	vw	3·685	vw	3·690	vw	3·698	vw
3·621	ms	3·618	ms	3·605	ms	3·614	s	3·617	s
—	—	—	—	—	—		—	—	—
—	—	—	—	—	—		—	—	—
3·458	wm	3·454	wm	3·444	wm	3·454	m	3·458	wm
3·405	vw	3·405	w	3·396	w	3·405	w	3·406	w
—	—	—	—	—	—	—	—	—	—
3·350	m	3·352	m	3·343	m	3·354	m	3·360	m
3·250	wm	—	—	3·257	wm ?	3·249	s	3·260	s
3·220	wm	3·230	ms	3·233	ms	—	—	—	—
3·192	vvs	3·194	vvs	3·185	vvs	3·196	vvs	3·204	vvs
3·165	s	3·168	s	3·163	vs	3·177	vs	3·181	vs
3·121	m	3·120	ms	3·113	s	3·120	ms	3·124	ms
3·016	wm	3·020	m	3·018	m	3·033	m	3·044	m
2·935	ms b	2·941	ms	2·934	ms	2·942	s b	2·946	ms b
—	—	2·924	wm	2·917	wm	—	—		—
*	—	2·894	w	2·888	w	2·893	vw	2·894	vw
—	—	—	—	—	—	—	—	—	—
2·648	wm	2·644	wm	2·638	wm	2·637	wm	2·645	wm
—	—	—	—		—	—		—	—
—	—	—	—		—	—	—	—	—
—	—	—	—	—	—	—	—	—	—
—	—	—	—		—	2·507	ms	2·520	ms
2·509	ms	2·506	ms	2·499	ms	2·491	ms	2·495	ms
—	—	—	—	—	—	—	—	—	—

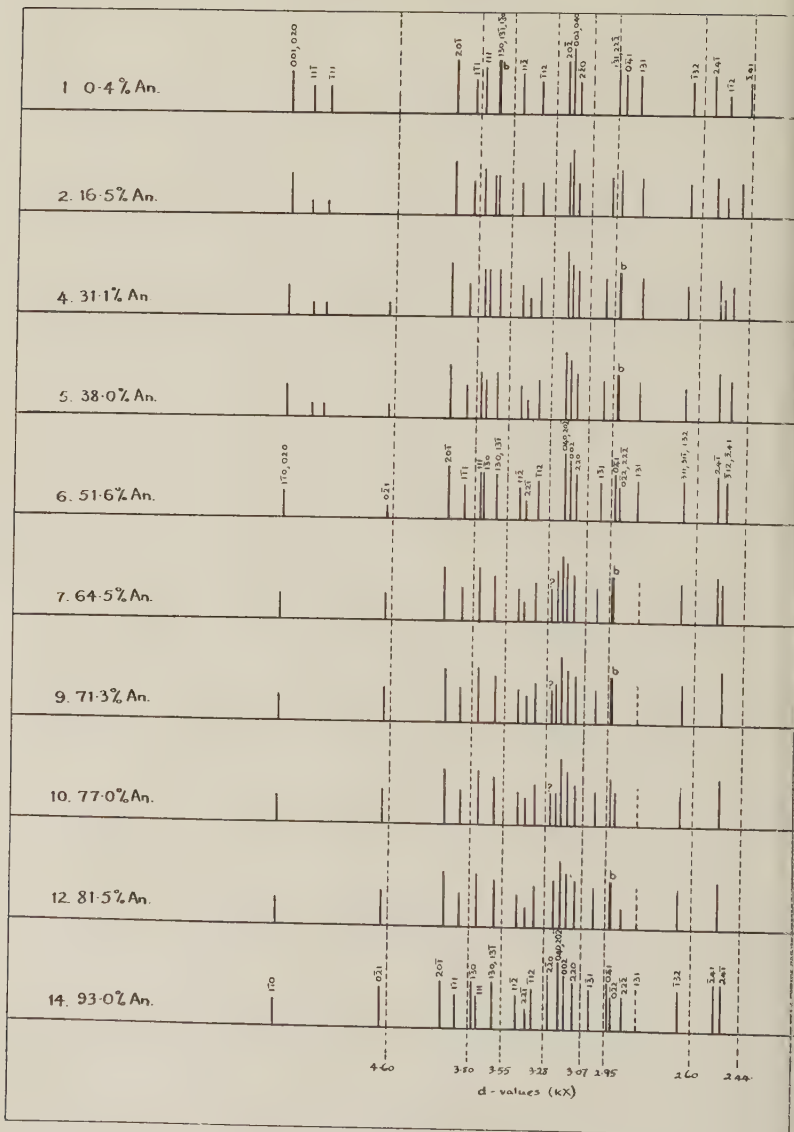


FIG. 1. Powder patterns of some natural plagioclases. Heights of lines represent relative intensities estimated visually. b, broad line or two unresolved lines; ?, exceptionally spotty; – – –, masked by calibration reflection of rock-salt.

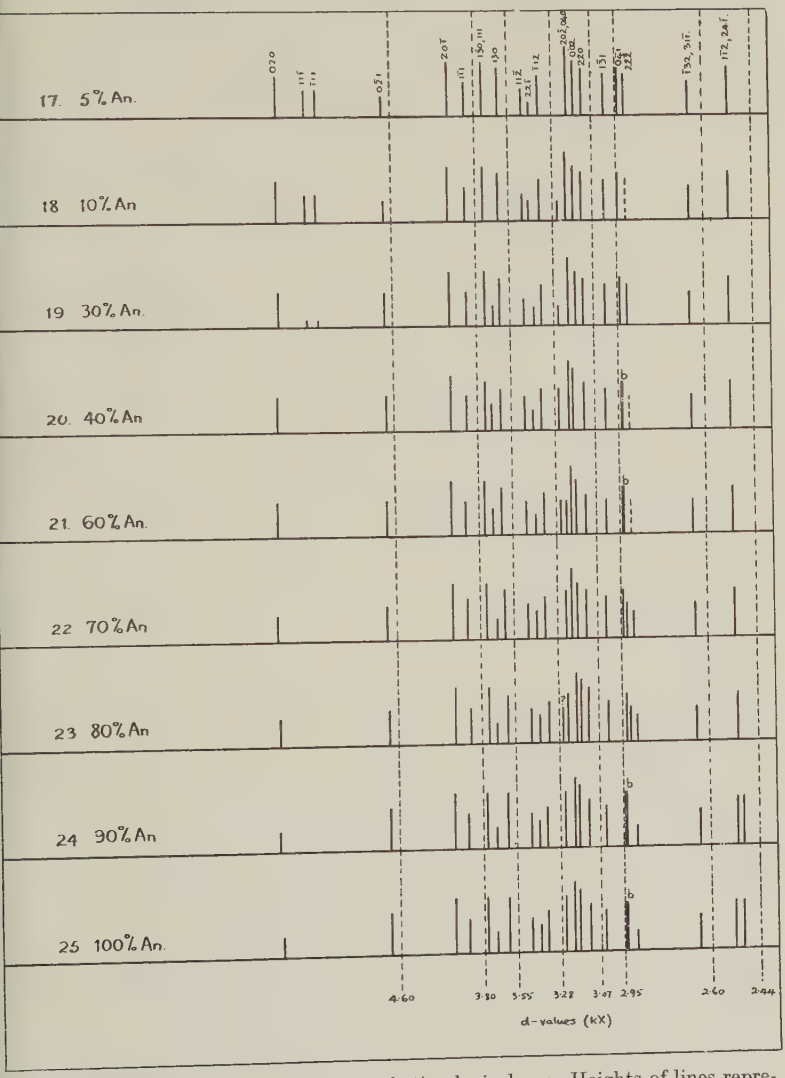


FIG. 2. Powder patterns of some synthetic plagioclases. Heights of lines represent relative intensities estimated visually. b, broad line or two unresolved lines; ?, exceptionally spotty; – – –, masked by calibration reflection of rock-salt.

quartz. All other observed lines which have been recorded are interpreted as typical plagioclase reflections. A diagrammatic representation of the patterns is given in figs. 1 and 2.

4. Diagnostic features of the X-ray patterns.

A plagioclase can usually be identified, and at the same time distinguished from an alkali-felspar, by the occurrence of the following characteristics in an X-ray powder pattern:

(i) two very strong reflections of spacing in the range 3·16–3·21 kX;
(ii) a medium reflection of spacing 6·4–6·5 kX;
(iii) three medium to strong reflections with spacings 4·02–4·04, 3·73–3·77, and 3·61–3·66 kX respectively.

An observation of other plagioclase reflections (see data given in tables III and IV) ought to establish its presence conclusively.

A detailed inspection of a plagioclase pattern would reveal several useful features enabling the material to be assigned to an approximate composition range, and in some cases providing information regarding its thermal modification. The most diagnostic portions of the patterns are indicated in figs. 1 and 2, and a description of the reflections occurring in them is given below.

Changes occurring in the character of the patterns are particularly prominent at the albite end of the series. On the basis of the patterns which have been indexed, it is evident that the differences are due mainly to the variation that occurs in the reciprocal lattice parameter γ^* of low-temperature albite on increasing the anorthite content, or on heat-treatment.

(*a*) 2·44–2·60 kX.—Natural albite gives three reflections of intensities, medium, weak, and weak-medium in order of decreasing spacing, but the weakest of the group, the $1\bar{1}2$ reflection of albite, is not observed in the patterns of natural materials with more than 40 % anorthite. Although the intensities of the stronger reflections (indices $24\bar{1}$ and $\bar{2}41$ for albite) remain practically unchanged, their separation decreases with increasing anorthite content up to 65 % anorthite, there remaining but one unresolved reflection within the range $An_{70}Ab_{30}$–$An_{90}Ab_{10}$. The synthetic materials give only one corresponding reflection over the whole range An_0Ab_{100}–$An_{80}Ab_{20}$.

Both high- and low-temperature materials of composition $An_{90}Ab_{10}$–$An_{100}Ab_0$ give two medium-strong reflections whose separation increases with increasing anorthite content, being about 0·03 kX for pure low-

temperature anorthite and somewhat smaller for synthetic anorthite. The presence of these reflections is sufficiently diagnostic to identify anorthites with certainty.

It appears that the $24\bar{1}$ and $\bar{2}41$ reflections of low-temperature albite shift towards each other as the anorthite content increases, crossing somewhere in the range $An_{70}Ab_{30}$–$An_{80}Ab_{20}$ and being again resolved at $An_{90}Ab_{10}$. Although they are not resolved for specimen 13 (86·5 % anorthite), there is an unusually broad line in the X-ray pattern suggesting that their spacings have different values for this composition.

(*b*) 2·95–3·07 kX.—In this region all patterns have one reflection, with probable indices $1\bar{3}1$, whose spacing for natural materials varies from 2·95 at An_0Ab_{100} to 3·00 kX at $An_{40}Ab_{60}$, and from 3·01 at $An_{70}Ab_{30}$ to 3·03 kX at $An_{100}Ab_0$. The spacing of the $1\bar{3}1$ reflection for synthetic albite is about 3·00 kX, significantly greater than the corresponding value for low albite. For the remaining synthetic materials the spacing increases but slightly with anorthite content up to $An_{80}Ab_{20}$, changing from 3·02 to 3·04 kX in the range $An_{80}Ab_{20}$–$An_{100}Ab_0$.

Tuttle and Bowen (1950) pointed out the diagnostic value of the $1\bar{3}1$ spacing in distinguishing between high- and low-temperature albites. The present data indicate that a distinction can be made on this basis for materials containing up to 40 % anorthite.

(*c*) 3·07–3·28 kX.—This region is characterized by the presence of the two very strong plagioclase reflections. In the pattern of natural albite the weaker of these has the higher spacing with indices $20\bar{2}$, the other having possible indices 040 and 002; there is also a third weak-medium reflection with indices $2\bar{2}0$. A similar group of lines is found in the pattern of oligoclase, specimen 2.

In the patterns of the natural materials of higher anorthite content, and in those of all the synthetics, there is a medium-strong reflection, with possible indices 220, corresponding in position to the $2\bar{2}0$ line of natural albite, but the stronger of the two very strong reflections is now of higher spacing and there occur one or two additional reflections of even greater spacing. These differences are probably due to changes in the 220, $2\bar{2}0$, and 040 spacings.

(*d*) 3·55–3·80 kX.—The strong, rather broad line given in this region by albite probably consists of three overlapping reflections with indices 130, $13\bar{1}$, and $1\bar{3}0$. In the pattern of specimen 6 (51·6 % anorthite), the 130 and $13\bar{1}$ reflections again coincide, but the $1\bar{3}0$ reflection, of weak-medium strength, now lies quite close to the 111 line, whose spacing is not very different from that in albite. For materials of

intermediate composition a line, apparently corresponding to the $1\bar{3}0$ reflection, has a spacing which increases with increasing anorthite content. This variation might be useful in determining the approximate composition of a low-temperature plagioclase of anorthite content less than 50 %.

In the pattern of natural anorthite, specimen 14, the 130 and $13\bar{1}$ reflections again coincide, but the $1\bar{3}0$ reflection is now of greater spacing and intensity than the 111.

The synthetic albites, specimens 17 and 18, give 111 and 130 reflections whose separation is of the order found for natural albite, but the $1\bar{3}0$ spacing coincides with the 111. For materials of higher anorthite content a third intermediate and weaker reflection is also recorded.

(*e*) 4·60 kX and above.—This region of the pattern is not very useful for indicating composition or distinguishing between high- and low-temperature forms. The characteristic 6·4–6·5 kX reflection is of medium strength for albites and oligoclases, but decreases in intensity as anorthite content increases, and there is a similar change in the intensities of the $11\bar{1}$ and $\bar{1}11$ reflections which become too weak to be observed in patterns of labradorites, bytownites, and anorthites.

Interesting features are: (i) the appearance of the $0\bar{2}1$ reflection for materials of anorthite composition greater than 30 %; (ii) the appearance in the patterns of natural bytownites and anorthites of a few very faint reflections of spacings greater than 4·03 kX, which are not of the type $(h+k)$ even. These may possibly be (*b*)-type reflections (see Gay, 1953), and are not considered here, since the relatively high background intensities of the patterns do not permit accurate measurement.

In view of the importance of high-spacing reflections for identification purposes, it is intended to study this region taking careful precautions to minimize the background of the pattern.

5. Quantitative estimation of composition from X-ray data.

In the preceding section certain plagioclase reflections whose positions vary in a systematic manner with composition have been described. By recording such reflections very accurately, a plot of their angular positions against composition would probably furnish determinative curves for plagioclase analysis. It is unlikely that the accuracy required can be achieved by the usual photographic methods of recording powder patterns, since many systematic errors, some of which vary with the nature of the powder specimen, are likely to arise. This difficulty can

be overcome by measuring the angular separation of two adjacent reflections rather than the absolute position of one line: the measurement is then almost independent of even relatively large calibration errors and is accurately reproducible by most powder techniques. This method has been used by Claisse (1950) and by Tuttle and Bowen (1950) for the plagioclase felspars.

If any useful relationship is to be established, it is necessary to use two reflections whose separation is sensitive to small compositional changes over the whole range, or at least a large part of it, and which are well defined and set apart from other lines. Claisse chose two groups, each consisting of three reflections, which satisfied many of these conditions. Those of one group, named 1, 2, and 3 by Claisse and referred to in this paper as C, D, and E respectively, lie in the spacing range 2·60–3·10 kX. Those of the second group, Claisse's 4, 5, and 6 lines, have much lower spacings, and though they lie in a complex region of the pattern, nevertheless the group as a whole is prominent and easily recognized: the 4

TABLE V. Details of the reflections.

Line.	Spacing (kX units).	Intensity.	Probable indices.
A	3·11 –3·14	wm–ms	$2\bar{2}0$ or 220*
B	2·95 –3·03	wm–ms	$1\bar{3}1$
C	2·63 –2·65	wm–m	$\bar{1}32$
D	2·50 –2·56	m-s	$24\bar{1}$
E	2·44 –2·52	wm–s	$\bar{2}41$
F	1·825–1·833	m–ms	—
G	1·764–1·785	ms	—

* $2\bar{2}0$ for low-temperature albite.

TABLE VI. Angular separations ($\Delta 2\theta^\circ$ for Cu-$K\alpha$ radiation) of the A B, C–D, C–E, and F–G reflections.

Natural plagioclases						Synthetic plagioclases					
No.	An. (wt. %).	A–B.	C–D.	C–E.	F–G.	No.	An. (wt. %).	A–B.	C–D.	C–E.	F–G.
1	0·4	1·85	1·06	2·81	1·20	17	5	1·09	1·90	—	1·54
2	16·5	1·63	1·34	2·51	1·39	18	10	1·10	1·91	—	1·54
3	22·1	1·51	1·44	2·38	1·50	19	30	1·07	1·91	—	1·58
4	31·1	1·35	1·61	2·22	1·53	20	40	1·04	1·93	—	1·68
5	38·0	1·31	1·63	2·21	1·61	21	60	1·02	1·93	—	1·84
6	51·6	1·25	1·69	2·14	1·71	22	70	0·97	1·93	—	1·91
7	64·5	1·14	1·79	2·06	1·84	23	80	0·92	1·94	—	2·01
8	66·3	1·09	1·80	2·03	1·85	24	90	0·84	2·05	1·82	2·06
9	71·3	0·99	1·90		1·87	26	100	0·77	2·11	1·75	2·12
10	77·0	1·01	1·89		1·91	(heated)					
11	81·0	0·96	1·92		1·91	26	100	0·77	2·15	1·77	2·02
12	81·5	0·96	1·92		1·92						
13	86·5	0·88	1·92		1·94						
14	93·0	0·81	2·13	1·80	1·95						
16 (volcanic)	~100	0·79	2·19	1·76	1·98						
15	98·3	0·76	2·14	1·78	2·03						

and 6 lines only are dealt with here, being referred to as F and G respectively. The precise descriptions of these reflections as they appear in the patterns of the natural materials are given in table V, together with another group of two, named A and B, which are also used.

By plotting against composition the angular separations, $\Delta 2\theta^\circ$, of the reflections in each of his two groups, Claisse obtained six linear relationships, each of which showed a break in the vicinity of $An_{30}Ab_{70}$–$An_{40}Ab_{60}$. The curves for the C–D–E combination were steeper than the others, but apparently suffered a disadvantage in that reflections D and E crossed each other at about $An_{80}Ab_{20}$, leading to some ambiguity in interpretation in this region. The F–G combination was free from this limitation, and the slope of the curve was sufficiently great to enable a reasonable estimate of composition to be made. By making use of all the curves the author claimed that, in general, it should be possible to estimate composition to 1 %.

Several objections can be raised to Claisse's work: (i) only eight plagioclases were used to cover the whole composition range, four of these lying within the limits An_0Ab_{100}–$An_{30}Ab_{70}$; (ii) all the materials were apparently assumed to be of low-temperature form, though the anorthite specimen came from a volcanic locality; (iii) all the analyses were based on optical measurements and compositions were claimed to be accurate to 1 %. Further, it is not clear from Claisse's paper whether or not each composition was determined on more than one grain. This is important, since presumably the powder specimens consisted of material representative of many grains. In the present work none of these difficulties arise, and an attempt has been made to describe in some detail the nature of the reflections employed.

The reflections A and B have been discussed in sections 4(*c*) and (*b*) respectively, and D and E in section 4(*a*), together with the corresponding reflections which appear in the patterns of the synthetic materials. The C reflection, with indices $\bar{1}32$ for natural albite, is similar in position and intensity in all the patterns. All these lines are sharp and can be readily recorded, the only complication occurring in the overlap of D and E in the patterns of natural materials of composition about $An_{80}Ab_{20}$.

Microphotometer traces of reflections F and G are shown in fig. 3, and from these it can be seen that the G peak is quite sharp for all specimens. While the F peak is reasonably resolved from neighbouring reflections for all the natural specimens, difficulties arise in its interpretation in the patterns of some of the synthetic materials. Specimens 20

and 21 show a diffuseness of the F peak which is certainly due to their poor crystallinity. In specimen 23 the peak is only just resolved from a neighbouring reflection of slightly larger spacing, and although specimen 24 apparently shows only one line in this region, the better crystallized specimen 26 quite definitely shows two. For this reason the pattern of the latter has been used to obtain the positions of the F and G reflections for synthetic anorthite.

Table VI contains the angular separations of the various combinations of reflections; the values, which are given for Cu-$K\alpha$ radiation to facilitate comparison with Claisse's data, are accurate to within $\pm 0{\cdot}03°$. Figs. 4, 5, and 6 show the curves obtained by plotting angular separations against composition determined chemically.

The A–B, C–D, and C–E curves for the natural materials each show prominent discontinuities reasonably close to the structural discontinuities at $An_{30}Ab_{70}$ and $An_{70}Ab_{30}$ proposed by Cole et al. (1951). These are significant as each of these reflections probably has the same, or similar, indices over the whole composition range. Although the break at $An_{30}Ab_{70}$ is very marked in each case, that at the calcic end appears to be more complex, and cannot be represented by the intersection of two straight lines. In the C–D and C–E curves the situation is further complicated by the failure to resolve the D and E reflections over an appreciable range of composition, and only tentative dotted lines can be used to represent the relationships from $An_{65}Ab_{35}$ to $An_{100}Ab_0$.

Corresponding curves for the synthetics show only one discontinuity at about $An_{75}Ab_{25}$. This is in harmony with the conception of a complete solid solution for high-temperature materials from An_0Ab_{100} to $An_{70}Ab_{30}$, which is suggested by the single-crystal diffraction work of Gay (private communication), although the early work of Bowen (1913) on melting phenomena indicated solid solution over the whole range from albite to anorthite.

The F–G curves for natural and synthetic materials, fig. 6, show slight discontinuities which cannot, in every case, be explained in terms of the structural scheme for the plagioclases, but since the F and G reflections occur in a more complex region of the pattern, it is possible that each does not have the same indices for all compositions.

By making use of selected portions of all the curves it should be possible to obtain reasonable analyses from X-ray data. The accuracy of an analysis so obtained will depend not only on the thermal history of the specimen but also on its composition.

(*a*) An_0Ab_{100}–$An_{30}Ab_{70}$. —The F–G separation enables a plagioclase

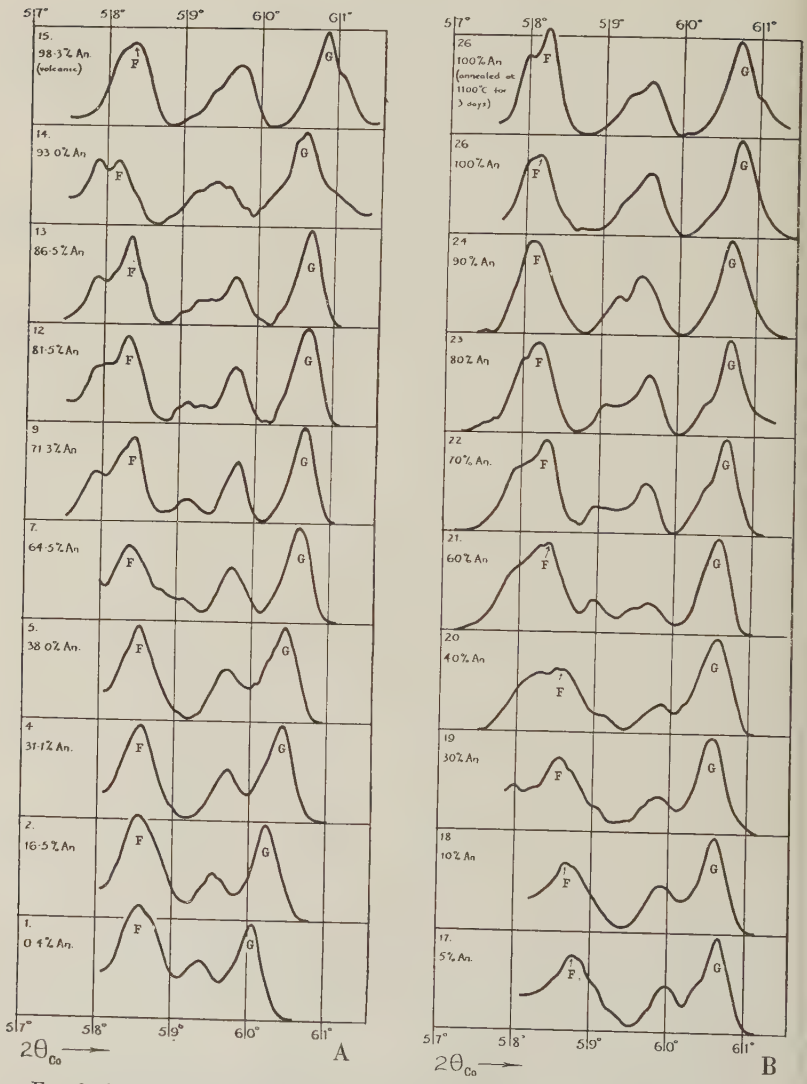


FIG. 3. Microphotometer traces of F and G reflections plotted for Co-$K\alpha$ radiation. G peak reduced to standard height. The 'annealed' no. 26 is discussed in section 5(*c*).

A, Natural plagioclases. B, Synthetic plagioclases.

o be assigned to this composition range. If the material is known to be f low-temperature form, the A–B, C–D, and C–E separations permit an accurate analysis to be made, since they are very sensitive to changes of composition. Although a high-temperature form can readily be recognized, there is no means of estimating its composition.

(*b*) $An_{30}Ab_{70}$–$An_{70}Ab_{30}$. —Using the A–B, C–D, and C–E curves, high- and low-modifications can be distinguished for compositions between $An_{30}Ab_{70}$ and $An_{65}Ab_{35}$, since a fairly good analysis can be obtained for both from the F–G curve.

At $An_{70}Ab_{30}$ there is practically no distinction between the characteristics of natural and synthetic materials; this was also found to be the case for specimen 9 when heated to 1250° C. for 48 hours.

(*c*) $An_{70}Ab_{30}$–$An_{100}Ab_0$. An estimate of the composition can be made using the A–B curve, but there seems to be no precise way of distinguishing between high- and low-temperature forms. The F–G curve might provide this information for compositions between $An_{90}Ab_{10}$ and $An_{100}Ab_0$, although not so conclusively as Gay's single-crystal method.

Two specimens are of interest in this connexion: (i) the synthetic anorthite 26, when 'annealed' at 1100° C. for three days, gives a well-resolved F reflection and an F–G separation of 2·02°, a value nearly falling on the natural curve; (ii) specimen 15, of volcanic origin, gives a separation of 2·03°, higher than the value expected of a low-temperature material of the same composition. The latter specimen thus appears to be partially inverted by this criterion.

According to the present data, the anorthite specimen employed by Claisse (1950) is clearly a high-temperature form. If this interpretation is correct, and it seems possible judging by the locality of this specimen, it is not surprising that Claisse failed to find discontinuities in his curves at $An_{70}Ab_{30}$.

6. Concluding remarks.

The identification of a plagioclase felspar is simplified by the fact that the general nature of the X-ray pattern does not vary considerably with either composition or thermal history. At the same time the pattern is sufficiently diagnostic to enable a fairly accurate analysis to be made over a wide range of composition. Further, a distinction can be made between high- and low-temperature modifications particularly in the range An_0Ab_{100}–$An_{40}Ab_{60}$, readily for $An_{40}Ab_{60}$–$An_{65}Ab_{35}$, and with some difficulty for $An_{90}Ab_{10}$–$An_{100}Ab_0$. For this purpose, the X-ray powder

method does not appear to be much superior to that based on optical data, according to a recent survey of the latter by Reynolds (1952).

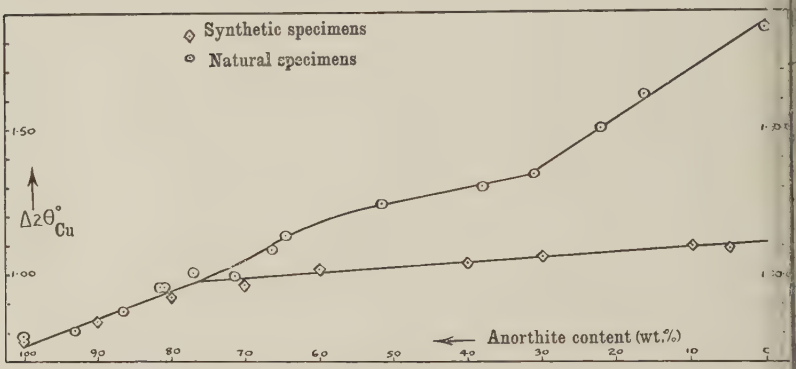


FIG. 4. Angular separation (calculated for Cu-$K\alpha$ radiation) of A–B reflections plotted against plagioclase composition.

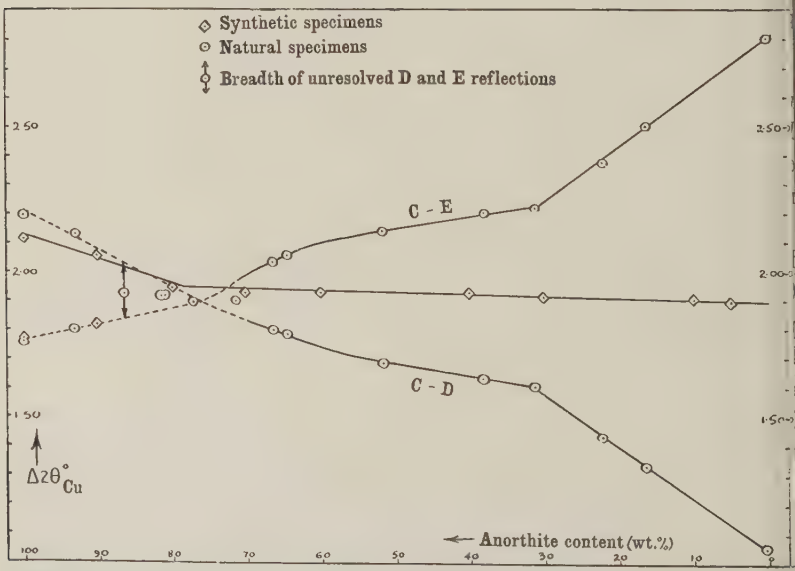


FIG. 5. Angular separation (calculated for Cu-$K\alpha$ radiation) of C–D–E reflections plotted against plagioclase composition.

The composition curves, figs. 4, 5, and 6, and their use in plagioclase analysis, cannot be taken as definitely established until their behaviour

as been studied in relation to heat-treated specimens. In this connexion implications are likely to arise from the possible occurrence of partially verted materials. Further experiments are now in progress to examine ese details.

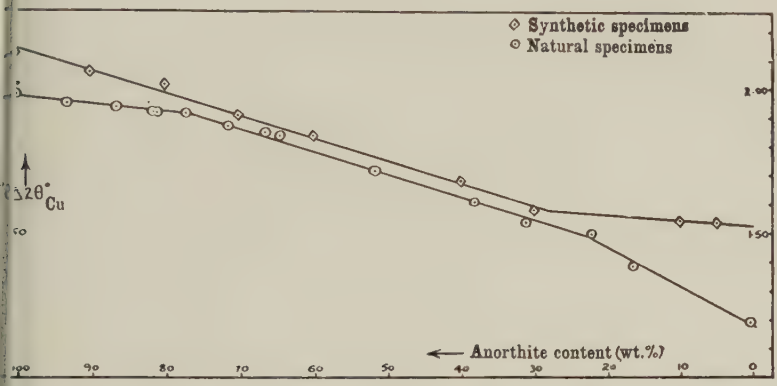


Fig. 6. Angular separation (calculated for Cu-$K\alpha$ radiation) of F–G reflections lotted against plagioclase composition.

The data presented in this paper show just how much can be done ith the usual powder techniques employing photographic recording. lore reliable data could no doubt be obtained by the modern Geiger ounter spectrometer, but such a refinement does not appear to be ecessary for the general problem of plagioclase identification.

Acknowledgements.—The authors wish to express their thanks to)r. W. H. Taylor (Cavendish Laboratory, Cambridge) and to Prof. . E. Tilley (Department of Mineralogy and Petrology, Cambridge) for roviding the materials used in this work. They are also indebted to)r. Taylor and Dr. P. Gay (Cavendish Laboratory) for much helpful liscussion, and to Prof. L. S. Palmer for his interest in this problem. Finally, thanks are due to the Royal Society for financial aid towards he purchase of equipment.

References.

Bowen (N. L.), 1913. The melting phenomena of the plagioclase feldspars. Amer. Journ. Sci., ser. 5, vol. 35, pp. 577–599.

Brindley (G. W.) and Robinson (K.), 1946. The structure of kaolinite. Min. Mag., vol. 27, pp. 242–253.

Chayes (F.), 1952. Relations between composition and indices of refraction in natural plagioclase. Amer. Journ. Sci., Bowen vol., pp. 85–105. [M.A. **12**-134.]

Claisse (F.), 1950. A roentgenographic method for determining plagioclases. Amer. Min., vol. 35, pp. 412–420. [M.A. **11**-428.]

Cole (W. F.), Sörum (H.), and Taylor (W. H.), 1951. The structures of the plagioclase felspars. I. Acta Cryst., vol. 4, pp. 20–29. [M.A. **11**–427.]

Donnay (G.) and Donnay (J. D. H.), 1952. The symmetry change in the high-temperature alkali-feldspar series. Amer. Journ. Sci., Bowen vol., pp. 115–132. [M.A. **12**–96.]

Emmons (R. C.), 1953. Selected petrogenic relationships of plagioclase. Mem. Geol. Soc. Amer., no. 52. [M.A. **12**–136.]

Gay (P.), 1953. The structures of the plagioclase felspars: III. An X-ray study of anorthites and bytownites. Min. Mag., vol. 30, pp. 169–177.

Kracek (F. C.), and Neuvonen (K. J.), 1952. Thermochemistry of plagioclase and alkali feldspars. Amer. Journ. Sci., Bowen vol., pp. 293–318. [M.A. **12**–134.]

Reynolds (D. L.), 1952. The difference in optics between volcanic and plutonic plagioclases, and its bearing on the granite problem. Geol. Mag., vol. 89, pp. 233–250. [M.A. **12**-137.]

Tuttle (O. F.) and Bowen (N. L.), 1950. High-temperature albite and contiguous feldspars. Journ. Geol., vol. 58, pp. 572–583. [M.A. **11**–327.]

pectrographic and X-ray data on some fluorites from the Transvaal, South Africa.

By J. G. D. Steyn, M.Sc.
Geological Survey, Pretoria, South Africa.[1]

[Taken as read November 5, 1953.]

I. Introduction.

THE fluorites of the Transvaal occur in different rock-types,[2] viz. in the dolomite of the Transvaal System, in acidic rocks (red granite d granophyre of the Bushveld igneous complex and Rooiberg felsites), d in alkalic rocks. The purpose of this study was to determine:

(1) What minor elements are present in selected fluorites.
(2) What the effect of these elements is on the respective cube-edges.
(3) Whether these elements have any geological significance.

Fluorite displays a wide range of colour; both colourless and distctly coloured specimens were examined. Differently coloured varieties uld in some instances be taken from the same sample. The choice of loured varieties in the different rock-types was nevertheless limited. nly light-coloured fluorites occur in the dolomite, whereas the alkalic cks yielded only very dark purple specimens.

II. Spectrographic examination.

A large Hilger Littrow type of spectrograph with a setting 2750–'00 Å. was generally used; only for Ge, Si, Te, P, and B was the setting ıanged to the range 2260–3000 Å. The material was arced between ›pper electrodes for 20 seconds at 5 amps; carbon electrodes were used r determining the rare-earths and copper.

Table I lists the analyses and other data. As the spectrographic sensivities of the elements differ greatly, the intensities should be used only ›mparatively for each separate element. No element is reported unless s presence was definitely established; conversely, failure to report an ement means that it was not present in a quantity above the limit of etection for the particular method used.

[1] Published by permission of the Honourable the Minister of Mines.

[2] L. E. Kent, H. D. Russell, and D. P. van Rooyen, Fluorspar in the Union of uth Africa and South West Africa. Bull. Geol. Surv. S. Africa, 1943, no. 14. I.A. 9–28.]

The common minor elements are: Fe, Mg, Sr, Cu, Al, Mn, Si, Sb, a
some of the rare-earths. Be, Pb, Na, P, and Ba are rare; the last
found only in a single specimen. The elements that could not be detec
in any of the samples are: Mo, In, Ga, Cd, Li, K, Rb, Cs, Bi, Hg, V, Z
Co, Ni, Cr, Ti, As, Zr, Nb, Pt, Os, U, W, Th, Ge, Te, B, Pr, Er, Sm,
Sn.

TABLE I. Spectrographic analysis of fluorites.
Estimated intensities using an arbitrary scale 0–10.

Sample no.	Fe.	Mg.	Be.	Sr.	Ba.	Al.	Pb.	Mn.	Na.	Cu.	Sb.	P.	Si.	Ce.	La.	Yt.	a at 25
1	3	4	3	4	—	2	—	1	—	1	—	—	1	—	—	—	5·46
2	—	3	—	—	—	—	—	3	—	2	—	—	—	—	—	—	5·46
3	3	3	—	1	—	3	—	1	—	2	1	—	1	—	—	—	—
4	5	4	—	10	—	6	—	3	—	3	—	—	4	—	1	2	5·46
5	7	3	—	10	—	4	—	6	1	—	—	2	6	1	1	1	5·46
6	3	2	4	3	—	3	—	2	2	—	1	—	5	1	2	—	5·46
7	1	2	—	1	—	1	1	1	—	—	—	—	—	—	—	—	5·46
8	1	2	—	7	—	3	—	3	—	—	—	—	5	—	—	—	5·64
9	1	3	—	—	—	2	—	—	—	—	1	—	—	—	1	—	5·46
10	8	3	—	10	—	4	—	4	—	3	1	—	3	—	—	—	5·46
11	—	4	—	5	10	1	—	—	—	—	2	—	2	—	—	—	5·46
12	1	1	—	—	—	1	—	1	—	—	2	—	1	1	—	—	5·46
13	2	1	—	—	—	2	—	—	—	—	3	—					—
14	—	3	—	—	—	2	—	—	—	4	—	—	—	1	—	—	—
15	3	3	—	2	—	2	5	3	—	1	2	—	2	—	—	—	—
16	5	1	—	—	—	3	6	—	—	3	—	—	2	—	—	—	5·46
17	4	2	2	3	—	2	—	1	—	—	2	—	—	—	—	—	5·46
18	3	2	—	4	—	2	—	2	2	4	2	—	—	1	—	—	—
19	1	5	1	5	—	4	1	—	—	—	—	—	7	—	—	—	5·46
20	2	1	—	—	—	—	—	1	—	10	?	—	—	—	—	—	—

1. Witkop 288, Marico district, Transvaal. Colourless. Dolomite.
2. Malmani Oog 101, Marico district. Colourless. Dolomite.
3. Malmani Oog 101, Marico district. Light purple. Dolomite.
4. Seekoeigat 287, Pretoria district. Very dark purple. Alkalic rock.
5. Leeuwfontein 320, Pretoria district. Very dark purple. Alkalic rock.
6. Cyferfontein 57, Warmbad district. Yellowish. Granite.
7. Groblershoek 785, Potgietersrust district. White. Granite.
8. Groblershoek 785, Potgietersrust district. Bluish-green. Granite.
9. Ruigtepoort 1373, Warmbad district. Colourless. Granite.
10. Houtenbek 392, Groblersdal district. Very dark purple. Granite.
11. Valsfontein 432, Groblersdal district. Green. Granite.
12. Zaaiplaats tin-mine, Potgietersrust district. Colourless. Granite.
13. Zaaiplaats tin-mine, Potgietersrust district. Greenish. Granite.
14. Zaaiplaats tin-mine, Potgietersrust district. Purple. Granite.
15. Mutue Fides tin-mine, Potgietersrust district. Light purple. Granite.
16. Stavoren tin-mine, Potgietersrust district. Purple. Granophyre.
17. Stavoren tin-mine, Potgietersrust district. Colourless. Granophyre.
18. Stavoren tin-mine, Potgietersrust district. Yellowish. Granophyre.
19. Synthetic fluorite.
20. Blank copper electrodes.

III. X-RAY EXAMINATION.

The X-ray work was carried out on a Seifert X-ray unit with u
filtered copper radiation. A Debeye-Scherre type of camera was e
ployed. The exposures were about $2\frac{1}{4}$ hours at 35 kV. and 20 mA. T
variation in temperature never exceeded 1° C. after certain precautiona
measures. The films were measured in triplicate after drying for a wee
the cube-edge was calculated after 2θ had been corrected for fi

shrinkage. The parameters tabulated in table II were derived by the extrapolation method of Bradley and Jay.[1] The following values, expressed in terms of (*hkl*), were used in constructing the graphs: (444), (533), (620), (531), (440), (511) $K\alpha 1$; (642) $K\beta$.

The exposures were all made within a temperature range 22°–27° C., and the results corrected to correspond to a mean temperature of 25° C. Taking the thermal expansion of fluorite as 0·16 % at 20–100° C. (Dana, 7th edit., 1951, p. 32), the expansion correction for the fluorite parameter is therefore 0·00012 A. per degree centigrade. The accuracy of the apparatus and the technique has been indicated by Wasserstein[2] of this laboratory. The results listed in table II, subject to a limit of error of 0·0005 Å., can therefore be regarded as precision measurements.

Synthetic fluorite was prepared by precipitating CaF_2 from $CaCO_3$ with hydrofluoric acid. This material yielded a very weak back-reflection pattern. After heating the precipitate in a crucible to a high temperature a perfect pattern was obtained; a 5·4627 Å.

Table II. X-ray data for fluorite from the Marico district, Transvaal.

No.	*hkl*.	Wave-length.	Int.	*d*Å. (meas.).	*d*Å. (calc.).
1	(111)	$K\beta$	5	3·149	3·154
2	(111)	$K\alpha_1$	10	3·150	3·154
3	(220)	$K\beta$	6	1·928	1·932
4	(220)	$K\alpha_1$	10	1·927	1·932
5	(311)	$K\beta$	2	1·646	1·647
6	(311)	$K\alpha_1$	9	1·642	1·647
7	(400)	$K\alpha_1$	4	1·364	1·366
8	(331)	$K\alpha_1$	5	1·251	1·253
9	(422)	$K\alpha_1$	8	—	1·115
10	(511)	$K\alpha_1$	3	1·050	1·050
11	(440)	$K\alpha_1$	3	0·964	0·966
12	(531)	$K\alpha_1$	4	0·922	0·923
13	(620)	$K\alpha_1$	6	0·864	0·864
14	(533)	$K\alpha_1$	4	0·834	0·833
15	(642)	$K\beta$	3	0·730	0·730
16	(444)	$K\alpha_1$	5	0·788	0·788
17	?	?	5		

No indices or spacing have been given to reflection no. 17. This highest back-reflection angle, with intensity the same as the (444) $K\alpha_1$ line, is most probably caused by interference of the (444) $K\alpha_2$ and (731) $K\beta$ lines. It gives a relatively high value for the cube-edge if taken as (444) $K\alpha_2$ and a relatively low value if taken as (731) $K\beta$.

[1] A. J. Bradley and A. H. Jay, Proc. Physical Soc. London, 1932, vol. 14, p. 563. [M.A. **5**–305.]

[2] B. Wasserstein, Amer. Min., 1951, vol. 37, p. 102. [M.A. **11**–316.]

The purest fluorites encountered in this study are those from th dolomite in the Marico district (samples 1 and 2); their parameter a 5·4626±0·0005 Å., at 25° C. The averages of their spacings are lis in table II.

IV. Discussion.

Although a large range of minor elements was detected spectrographic ally, substitutions likely to affect the cube-edge, after allowing for error were encountered in only three samples. The ionic radii of some of th minor elements and that of Ca are: Mn″ 0·91, Na′ 0·98, Ce‴ 1·18 (1·0 La‴ 1·22 (1·04), Yt‴ 1·06, Ca″ 1·06, Sr″ 1·27, Ba″ 1·43 kX. Due t similarity in size, replacements of Ca″ may occur in the fluorite struct without affecting the cube-edge to any measurable extent.

Samples 4, 5, and 10 show an increase in the cube-edge of at lea 0·0055 Å. as compared with pure CaF_2. *These three are all very dar purple in colour and contain an appreciable amount of strontium.* Th large amount of strontium present in these fluorites was the mo significant result of the spectrographic analyses. Chemical analys confirm these findings (table III). The highest cube-edge sample, vi 5, contains over 1 % strontium, whereas the other samples, with norma cube-edges, contain virtually no strontium. The Sr″ ion is larger tha the Ca″ ion. Furthermore, SrF_2 has a greater cube-edge (a 5·86 Å.) tha CaF_2. The results therefore prove that the replacement of Ca″ by Sr in fluorite causes an appreciable enlargement in the size of the fluorit cell.

Table III. Chemical analyses of fluorites. (Numbers as in table I.)

			5.	1.	6.
CaO	...	...	71·66	71·55	69·62
SrO	...	...	1·34	0·05	trace
MgO	...	...	0·008	0·012	0·008
MnO	...	...	0·005	—	—
Na_2O	...	...	0·02	—	0·02
FeO	...	...	0·04	0·04	0·03
SiO_2	...	...	0·03	—	0·28

Analyst: C. van Rooyen. High CaO in no. 5 due to presence of apatite.

The presence of contaminating minerals in fine cracks in the fluorit host (fig. 1) or as inclusions (fig. 2) has an influence on the minor elemen content of fluorite; lead was found, for example, in samples 15 and 1 which are accompanied by galena; phosphorus was encountered onl in the Leeuwfontein fluorite (no. 5), which occurs with apatite.

The large amount of barium found in sample 11 is due to the contamination of baryte, a mineral accompanying this fluorite. If $Ba^{"}$ had replaced $Ca^{"}$, the larger ionic size of the former would have caused a remarkable increase in the cube-edge of this particular fluorite. Because of the difference of 0·37 kX in their ionic size it is also unlikely that $Ba^{"}$ would ever replace $Ca^{"}$: "Generally speaking, it may be stated that the ion (*A*) may replace the ion (*B*) diadochically if the difference in size of their radii does not exceed about 15 % of the radius of (*B*)."[1] In this example the difference is about 35 %.

FIG. 1

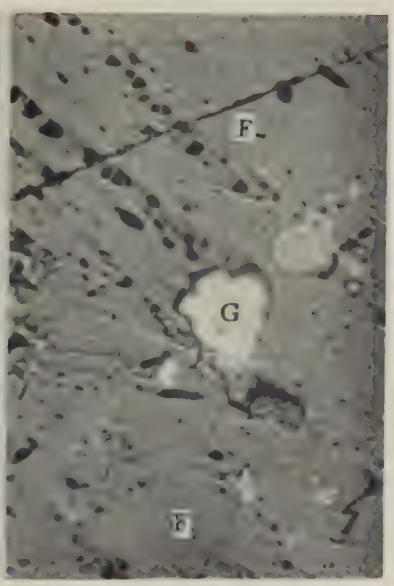


FIG. 2

FIG. 1. Photomicrograph showing chalcopyrite (Cp) along a microscopically fine fracture in fluorite (F) with quartz (Q). Magnification × 160.

FIG. 2. Photomicrograph showing inclusions of galena (G) in fluorite (F). Magnification × 56.

There exists a relation between the minor elements of fluorite and the country-rock in which the mineral was deposited. The fluorites occurring in the alkalic rocks contain larger quantities of impurities, whereas those occurring in the dolomite are purer.

[1] K. Rankama and T. G. Sahama, Geochemistry, Chicago, 1950, p. 122. [M.A. **11**–409.]

Except for the relatively large amount of strontium present only i the very dark purple fluorites, an attempt to correlate the colour of t fluorites with their minor element content was not successful.

Addendum.—The above results were obtained prior to the publicat by R. D. Allen, Variations in the chemical and physical properties fluorite. (Amer. Min., 1952, vol. 37, p. 910.) [M.A. **12**, 161]. He repor *a* 5·46295±0·00010 Å., at 28° C. for a synthetic fluorite of optic grade. If this value is corrected to correspond to a temperature of 25° C it becomes *a* 5·4626 Å., which is identical with the value found for t fluorites of the Marico district.

A simple monochromator.

By H. C. G. Vincent, M.A.
Department of Mineralogy and Geology, University of Cape Town.

[Communicated by Dr. G. F. Claringbull; read June 11, 1953.]

An easily constructed apparatus, giving illumination by light of any chosen colour, and of adequate purity in a narrow spectral region, has been made and found satisfactory in the determination of the optical properties of crystals.

Light of high intensity is focused on an adjustable slit, rendered approximately parallel by means of a lens, and passed through two hollow prisms containing alpha-monochloronaphthalene. In the widely divergent spectral beams the microscope moves along a calibrated arc and any desired wave-band of reasonable purity may be selected. The apparatus is illustrated in the accompanying diagram (fig. 1) and photograph (fig. 2).

A small carbon arc (*A*) using direct or alternating current gives adequate intensity, allowing for a narrow setting of the slit, with corresponding purity of the monochromatic beam. A lamp (as shown in the photograph) fitted with a 500-watt projection bulb is more convenient and satisfactory for most purposes, and, with a wider slit setting, even lower power may be used, but at the expense of purity of the required spectral colour. A heat filter should be interposed between the light source and the slit.

The white light, well screened, is concentrated by a lens (*B*) on to the adjustable slit (*C*) which is about $\frac{1}{2}$-inch long, fitted into the end of a 10-inch tube. A lens (*E*) of 4 inches focal length is centred and cemented into a wooden plug which slides in this tube and is adjusted into position later. The hollow prisms (*F* and *G*) are made from 4-inch squares of $\frac{1}{4}$-inch plate glass, and $4\frac{1}{2}$-inch triangles for the base and lid. The squares for the sides are accurately bevelled at 30° on two opposite edges, utilizing a 30° wooden block for the purpose, cemented together with a paste of very finely ground glass, sodium silicate, and a little zinc oxide; temporarily bound together by tape and kept at 30° C. for several hours. Each prism is then ground and cemented to its base and ground to take its lid. The prisms are charged with alpha-monochloronaphthalene. This liquid is relatively cheap and stable, has a high dispersion

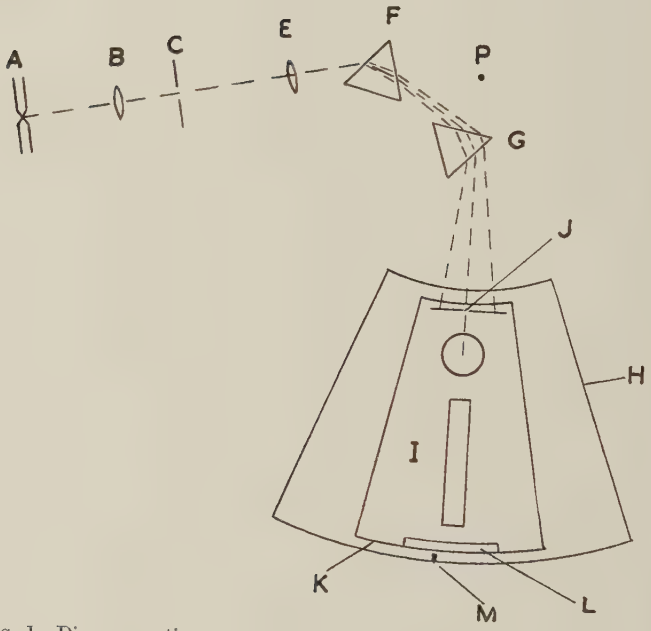


FIG. 1. Diagrammatic arrangement of the apparatus. (About one-tenth actual size.)

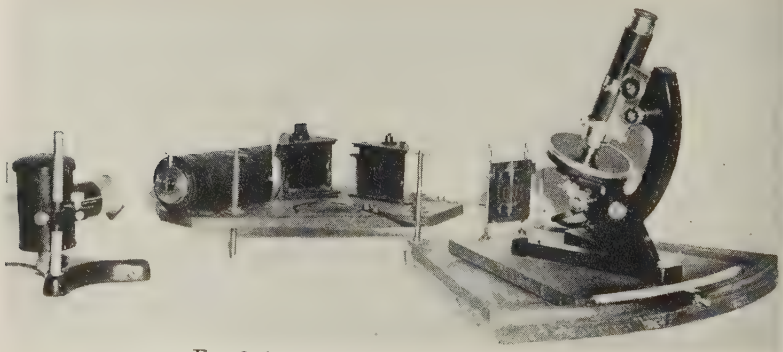


FIG. 2. Photograph of the monochromator.

$n_F - n_C = 0{\cdot}03$), low inflammability and vapour pressure (B.P. 259° C.). Any yellow discoloration should be removed by shaking with activated charcoal and filtering. The prisms, after charging, are fitted with their triangular lids, using a temporary seal such as glycerine and starch, and are blackened on the outside, leaving windows for the passage of the light beam.

The tube and prisms are fixed on one board carrying a spirit level, fitted with vertical screws allowing the height of the assemblage to be varied. The prisms are held in place, but removable, and arranged in the approximate position of minimum deviation for the middle of the green band. They are covered with a black metal hood, which is not shown in the photograph.

Where only a visual estimate of the colour and wave-band required is adequate, the apparatus may be used without addition. The microscope with mirror is placed in the beam and adjusted in position for the colour required, the intensity and purity being varied by the slit. The arrangement described below increases the scope and convenience of the apparatus, for the wave-lengths utilized are known within fairly narrow limits, or may be selected immediately by reference to a scale.

A stationary base-board (*H*), fitted with a rim, carries a moving platform (*I*), which may be locked in any desired position, on which the microscope is squarely placed. The platform is free to move in a circular arc such that any given point on it describes a circle whose centre lies at the origin (approximate) of the diverging beams when projected backwards (point *P*). To fulfil this requirement, the top of the base-board is fitted with two steel strips on edge, bent to the correct curve, which serve as rails, and engage with small wheels let into the under part of the sliding platform. A distance of about 12 inches from the microscope mirror to the nearest prism is found most satisfactory, and the radii of the curve of the inner and outer rail are fixed accordingly.

The prism-board and the base-board are linked by two steel arms; one end of each is bolted to the prism-board, the other ends being drilled and passing over vertical round posts on the corners of the base-board. In this way correct angular relationship between the prisms and the base-board is maintained, at the same time allowing for vertical adjustments of the prism assemblage to accommodate different light sources and easy dismantling. At the end of the platform an adjustable slit (*J*) in a large frame, capable of vertical movement, is centrally placed to intercept the coloured beams. On the face of the frame, which is painted white, the spectral bands and lines may be seen, and as the slit moves with the

platform and microscope, any given wave-band may be selected to pass through the slit to fall squarely on the microscope mirror.

On the curved vertical edge of the platform nearest the observer, which should be exposed about $\frac{1}{2}$-inch above the top of the rim of the base-board, a millimetre scale (K) is attached, and along the horizontal surface of the platform a curved white sliding scale (L) is so arranged that readings on the millimetre scale may be referred to wave-lengths marked on the sliding scale after calibration. Both these scales, which move with the platform and its microscope, may therefore be read with reference to a mark (M) on the base-board against the millimetre scale.

To calibrate the instrument, both the collimator and platform slits are nearly closed, and the arc carbon is moistened with sodium chloride. The lens in the tube is now adjusted into permanent position, to give the sharpest image of the sodium D-line on the white frame of the platform slit. The slit itself is now brought exactly over the D-line and the reading on the millimetre scale noted; the prominent lines of thallium and lithium salts are read in a similar manner.

The lines are most clearly seen if all extraneous light is excluded and the arc carbons are separated rather widely. Wave-lengths in microns, most easily recognized and adequate for calibration, are those of lithium 0·6104 (reddish-orange), 0·4602 (violet), sodium 0·5890–96 (yellow), and thallium 0·5351 (green). If flame spectra are used, the spectral line should be brought into view through the platform slit. The sharpness and purity are increased by a long-focus lens placed near the prism, but this has been found to be unnecessary; if it is fitted, it must not be moved after calibration.

A curve is constructed relating scale readings to the wave-lengths utilized together with wave-lengths in common usage such as the F-, E-, and C-lines, which are transferred from the curve on to the sliding scale.

Readings are thus made virtually independent of variables such as temperature changes, microscope mirror position, slit openings, &c. In using the instrument under a given set of conditions, the platform slit and D-line are made to coincide, and the microscope and mirror properly adjusted to receive the light. The sliding scale is then moved until the D-line calibration coincides with the reference mark on the base, and for this set of conditions the readings will be found to be correct for any other wave-lengths selected.

For a reasonably accurate setting of the instrument it is usually sufficient to adjust the yellow band over the platform slit, and it is not necessary to see the D-line itself. For refractive index work and similar

optical studies the essentially parallel light given by the instrument is particularly suitable, giving strong Becke-line effects, with or without condensers. With convergent light for interference figures, requiring higher intensity, wider slit openings are necessary, and the light should be diffused just before entering the condenser.

With good facilities the instrument without lamp may be made and calibrated in three or four days at a cost of about £5 for materials.

The identity of jurupaite and xonotlite.

By H. F. W. Taylor, B.Sc., Ph.D.

Department of Chemistry, University of Aberdeen.

[Read January 28, 1954.]

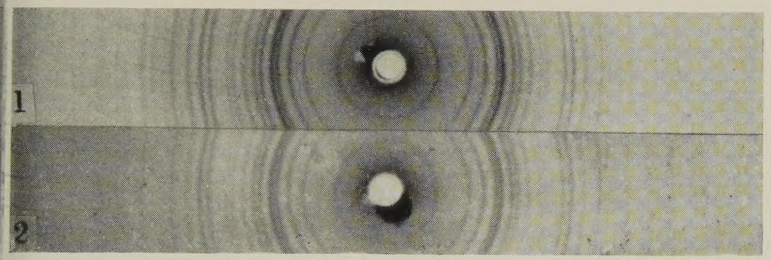
JURUPAITE was discovered at Crestmore, California, by A. S. Eakle[1] in 1921. The mineral was found in a quarry which was rapidly being enlarged, and Eakle stated that it was probably represented only by the one specimen which he had collected. He showed that it was a hydrated calcium silicate containing magnesia, with the composition $2(Ca,Mg)O.2SiO_2.H_2O$, the ratio of lime to magnesia being approximately 7:1.

This specimen passed into the keeping of Professor A. Pabst, who kindly made a portion available to the writer. He confirmed that it was unlikely that any other specimen existed. The jurupaite consisted of rosettes of white needles or fibres, about a centimetre in diameter. A brown discoloration was observed on the exposed outer surfaces of the specimen, but not on freshly cut surfaces. Calcite was present in contact with the jurupaite. Under the microscope, the material was seen to consist of aggregates of fibres, sometimes in approximately parallel orientation and showing parallel extinction and positive elongation; α 1·576, γ 1·583, both $\pm$0·005. Due to the small size of the individual crystals, the true extinction angle and optic sign could not be determined. These observations agree with the original description.

X-ray oscillation and rotation photographs about the fibre axis, and also a powder photograph (fig. 1) were obtained. The fibre photographs confirmed that the material consisted of aggregates of very small crystals, having their needle axes approximately parallel but oriented at random around this axis. Nearly all of the reflections could be indexed on a cell having a 8·50, b 7·32, c 7·05 Å., orthorhombic or monoclinic with β 90 $\pm$1°; marked pseudo-halving of b, which is the needle direction. A few weak reflections on the first layer-line could not be indexed on these axes, and the above cell is therefore probably a pseudo-cell rather than the true cell. Unfortunately, due to the fibrous nature of the material, the latter could not be determined.

[1] A. S. Eakle, Amer. Min., 1921, vol. 6, p. 107. [M.A. 1–253.]

Comparison of the X-ray photographs with corresponding ones of other hydrated calcium silicate minerals indicated identity with xonotlite ($3CaSiO_3.H_2O$). The specimen of xonotlite that was used came from the type locality, Tetela de Xonotla (or Tetela del Oro), state of Puebla, Mexico, and was kindly provided by the Building Research Station, Watford, Hertfordshire. It consisted of tough, white material, made up of interlaced fibres with parallel extinction and positive elongation;



FIGS. 1–2. Powder photographs of jurupaite and xonotlite. 1. Jurupaite, Crestmore, California; original specimen collected by A. S. Eakle. 2. Xonotlite, Tetela de Xonotla, Mexico. Both photographs were taken using a 6 cm.-diameter camera with filtered copper radiation, Cu-$K\alpha$, 1·542 Å. (Reproduced same size.)

α 1·581, γ 1·590, both $\pm$0·005. As in the case of the jurupaite, the true extinction angle and optic sign could not be determined. These data agree with those given previously for xonotlite from the same locality by E. S. Larsen.[1] The X-ray powder photograph (fig. 2) is identical with that of jurupaite, and gave data agreeing with those reported earlier for xonotlite from Puebla by W. T. Schaller;[2] closely similar data for xonotlite from other sources have been recorded by several other investigators. X-ray oscillation and rotation photographs about the fibre axis agreed closely with those of jurupaite, but showed even less orientation of the crystals within each fibre. The odd layer-lines were weaker relative to the even ones than in the case of jurupaite, suggesting that disorder existed also within the crystals. With the same exceptions, which in this case were extremely weak, the reflections could be indexed on the same cell or pseudo-cell (a 8·50, b 7·32, c 7·05 Å., β 90$\pm$1°) as was found for jurupaite. These dimensions agree closely with those (a 8·55, b 7·34, c 7·03 Å., monoclinic with $\beta \approx 90°$) found by H. Berman[3] for xonotlite from Franklin, Sussex County, New Jersey.

[1] E. S. Larsen, Amer. Min., 1923, vol. 8, p. 181. [M.A. **2**–253.]

[2] W. T. Schaller, Ibid., 1950, vol. 35, p. 911. [M.A. **11**–187.]

[3] H. Berman, Ibid., 1937, vol. 22, p. 342. Same work quoted by C. Palache, Prof. Paper U.S. Geol. Survey, 1935, no. 180, p. 113. [M.A. **6**–261.]

TABLE I. Data for jurupaite and xonotlite.

	Jurupaite (Crestmore) (Eakle, 1921).	Xonotlite (St. Inez) (Larsen, 1917).
Optical properties:		
Extinction	31° to elongation	‖ elongation
Sign of elongation ...	positive	positive
Optic sign	positive	+(biaxial, very low 2V)
n ‖ elongation	1·576±0·002	1·593±0·001
n ⊥ elongation	1·568±0·002	1·583±0·001
Birefringence	0·007	0·010
Other properties:		
Specific gravity	2·75	2·685–2·705
Hardness	4 approx., across fibres	6½
Fusion	2, to a clear white glass	2·5, to a glass
With dilute HCl ...	Soluble, no gelatinization	Soluble. SiO_2 separates without gelatinization
Loss of water	'Held tenaciously'	'Only at a high heat'
Chemical analyses (each mean of two analyses):		
SiO_2	48·87	50·17
Fe_2O_3	—	1·04
CaO	38·66	45·45
MgO	4·19	trace
H_2O	7·89	3·18
	99·61	99·84

Unit-cell or pseudo-cell:

	This investigation		
	Jurupaite (Crestmore).	Xonotlite (Tetela de Xonotla).	Berman, 1937 Xonotlite (Franklin).
a	8·50 Å.	8·50 Å.	8·55 Å.
b	7·32	7·32	7·34
c	7·05	7·05	7·03
β	90°±1°	90°±1°	90° approx.

The X-ray data thus show that jurupaite and xonotlite are the same species, although in the case of jurupaite part of the calcium is replaced by magnesium. The chemical analyses, cell-dimensions, and optical and other properties reported for jurupaite are compared in table I with representative data for xonotlite. As far as possible, these relate to a single specimen, from 'St. Inez' (Santa Ynez, Barbara County), California, which was chosen because all the required data, except for the cell-dimensions, were available for it.[1] The discrepancies between

[1] E. S. Larsen, Amer. Journ. Sci., 1917, vol. 43, p. 464. [M.A. **1**–206.] The material was originally described as 'eakleite' and was later shown to be xonotlite (Larsen, loc. cit., 1923).

urupaite and xonotlite are mostly small, and the lower indices of juru-
aite, at least, can reasonably be attributed to the partial replacement
f lime by magnesia.

Some uncertainty exists regarding the water content of xonotlite. The ideal formula, which alone appears compatible with the cell-dimensions and density, is $3CaSiO_3 . H_2O$, as already noted by Berman.[1] Most analyses, however, indicate lower water contents, and the formula $5CaSiO_3 . H_2O$ has often been assigned. In the case of jurupaite, on the other hand, the water content is higher than the ideal value. Further investigation seems desirable. The name xonotlite[2] has priority.

[1] H. Berman, Amer. Min., 1937, vol. 22, p. 342. Same work quoted by C. Palache, Prof. Paper U.S. Geol. Survey, 1935, no. 180, p. 113. [M.A. **6**–261.]

[2] C. F. Rammelsberg, Zeits. Deutsch. Geol. Gesell., 1866, vol. 18, p. 33. The original spelling was 'xonaltit'.